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Synthesis and Characterization of Functionalized Poly(arylene ether sulfone)s using Click Chemistry

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SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED POLY (ARYLENE ETHER SULFONE)S USING CLICK CHEMSITRY

A thesis submitted in partial fulfilment of the

requirements for the degree of

Master of Science

By

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B.sc Osmania University, 2010

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Wright State University

WRIGHT STATE UNIVERSITY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MYSUPERVISION BY Kavitha Neithikunta ENTITLED Synthesis and Characterization of Functionalized Poly(arylene ether sulfone)s using Click chemistry BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

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ABSTRACT

Neithikunta, Kavitha M.S., Department of Chemistry, Wright State University, 2016. Synthesis and Characterization of Functionalized Poly(arylene ether sulfone)s using Click Chemistry

Poly(arylene ether sulfone)s with pendent aryl iodide group was successfully synthesized via Nucleophilic aromatic polycondensation of 1-(3,5-difluorophenyl sulfonyl)-4-iodobenzene using 4,4'-difluorodiphenylsulfone (DFDPS) and Bisphenol A in the ratio 25:75:100. Iodo monomer was prepared by reacting 3,5-difluorodiphenyl sulfone with *N*-iodo succinimide (NIS). Using GC/MS and NMR spectroscopy, the quantitative analysis was done to this monomer. Modification was done to iodo copolymer using sodium azide and copper sulfate as catalyst to form azide copolymer. Further modification of the azide copolymer to triazole copolymers via Click Chemistry using different alkynes such as 1-octyne, phenyl acetylene, propargyl alcohol and acetylenedicarboxylic acid. Polymers characterization was done using ^{1}H, ^{13}C NMR, IR spectroscopy and SEC. The highest molecular weight (M_w) was found to be 19,033 Da with a PDI 3.0 for iodo copolymer and the least was found to be 6,888 with a PDI 2.5 for acetylenedicarboxylic acid derivative copolymer. Thermal analysis of polymers was done using TGA and DSC. The $T_{d5\%}$ values were ranging from 260^{o} to 476^{o}. The highest T_g was 191^{o} for phenyl derivative copolymer and the least was 174^{o} for alkyl derivative copolymer. TGA was not ran on azide copolymer as it may contain explosive copper azide traces. IR spectroscopy was used to confirm the structures of azide copolymer, propargyl alcohol derivative and acetylenedicarboxylic acid derivative copolymers.

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INTRODUCTION

1.1 Poly (arylene ether)s

Poly (arylene ether)s, PAEs, are a type of thermoplastic with good mechanical and chemical properties. A generic structure of poly (arylene ether)s can be represented as in **Figure 1**. They are high performance engineering thermoplastics with a wide range of applications such as the aerospace, automotive, electronics and related markets.[1] PAEs have excellent resistance to hydrolysis and oxidation, in addition to possessing relatively high glass transition temperatures, T_g. As a result of these properties, different functional groups can be introduced to these systems to meet the requirements for specific applications and also to maintain their excellent properties. PAEs are commonly prepared via nucleophilic aromatic substitution although they can also be prepared via electrophilic aromatic substitution.

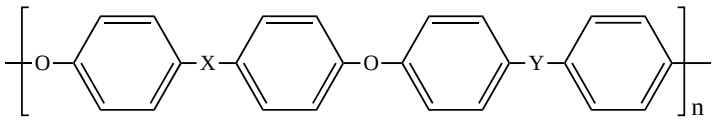


Figure 1. General representation of poly (arylene ether) backbone structure.

The structures, trade names and thermal properties of some common, commercially available PAEs including poly(phenylene oxide), PPO**,** poly(ether ether ketone), PEEK, and poly(arylene ether sulfone), PAES, [2, 3] are as shown in **Figure 2**.

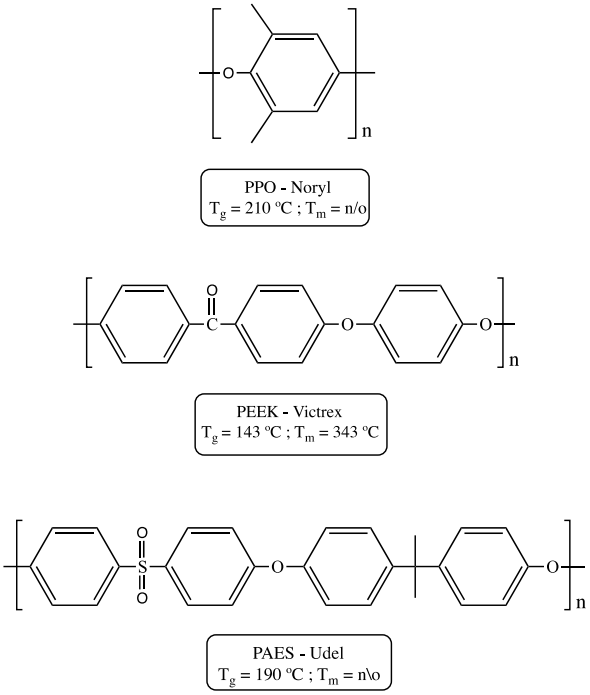
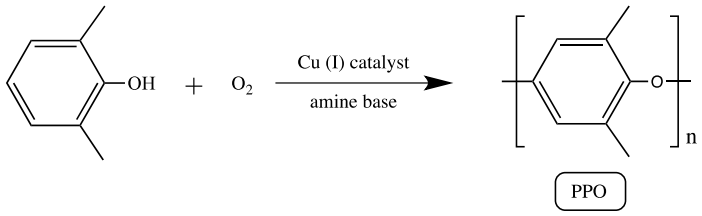


Figure 2. General structures, trade names and thermal properties of some commercial PAEs.

1.1.1 Poly(phenylene oxide), PPO

PPOs are polyethers with the aromatic rings connected by the oxygen linkages either at the *ortho* or *para* position or both positions in the backbone. This aromatic backbone contributes mainly to its high temperature and tensile strength. As the structure contains the repeat units and inherent stiffness, results in an amorphous polymer with the glass transition temperature (T_g) of 215°C.[4] PPO is an important engineering thermoplastic synthesized by oxidative coupling polymerization of 2, 6-dimethylphenol in the presence of cuprous (I) chloride catalyst and an amine base[5-8] as shown in **Scheme 1**.



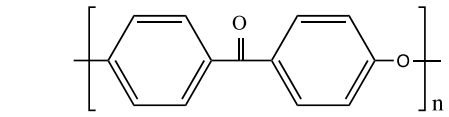
Scheme 1. Oxidative coupling of 2,6-dimethylphenol to form poly (phenylene oxide), PPO.

PPO shows a lower water absorption rate when compared to the other engineering thermoplastics at both room temperature and elevated temperatures.[1] Due to these properties, PPOs have many applications such as automotive industry, business machine cases, electrical components and gas separation membranes.[5] Although PPO exhibits excellent properties and many applications, its uses have been restricted due to its high processing cost. To reduce the cost of PPO it is mixed with polystyrene to produce polymer blends, which are commercially available in the name of Noryl®. This product will also have the same excellent properties as PPO.[1]

1.1.2 Poly(ether ether ketone)s, PEEK

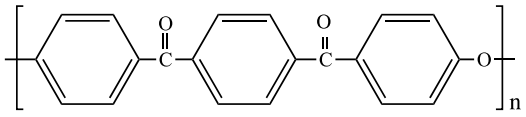
PEEK is a high performance, engineering thermoplastic consisting of a linear structure that contains aromatic rings with ether bridges and ketone moieties in the backbone. PEEK is semi-crystalline with a T_g of 143^o and melting temperature (T_m) at 343^o. PEEK has very desirable properties like thermal stability, chemical and solvent resistance, good mechanical properties, excellent fire resistance, low water absorption, electrical performance and resistance to acids and bases. Due to all these properties, PEEK has several industrial applications like coating and insulation for high performance wiring in aerospace and computers, military equipment, nuclear plant applications and oil wells

and engines with high operating systems.[9] Some of the common available poly (aryl ether ketone)s, PAEK, include poly (ether ketone), PEK; poly(ether ketone ketone), PEKK **;** poly(ether ether ketone), PEEK and other combinations as shown in **Figure 3.** PEEK, PEKK are the most widely used PAEK materials among all these high performance polymers.[10-14]



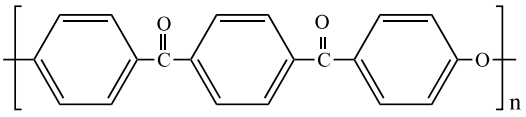
PEK

T_g = 163 °C ; T_m = 361 °C



PEKK

T_g = 165 °C ; T_m = 391 °C



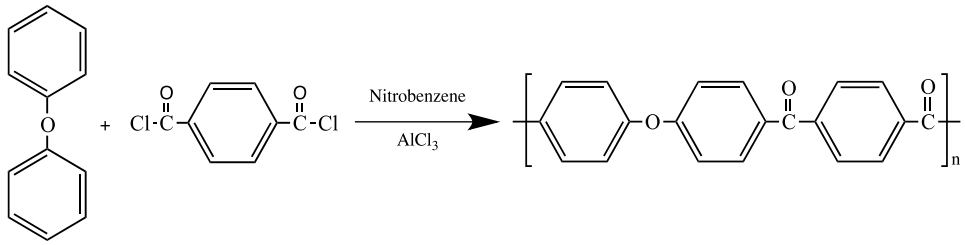
PEEK

T_g = 144 °C ; T_m = 344 °C

Figure 3. Structures of PEK, PEKK, PEEK

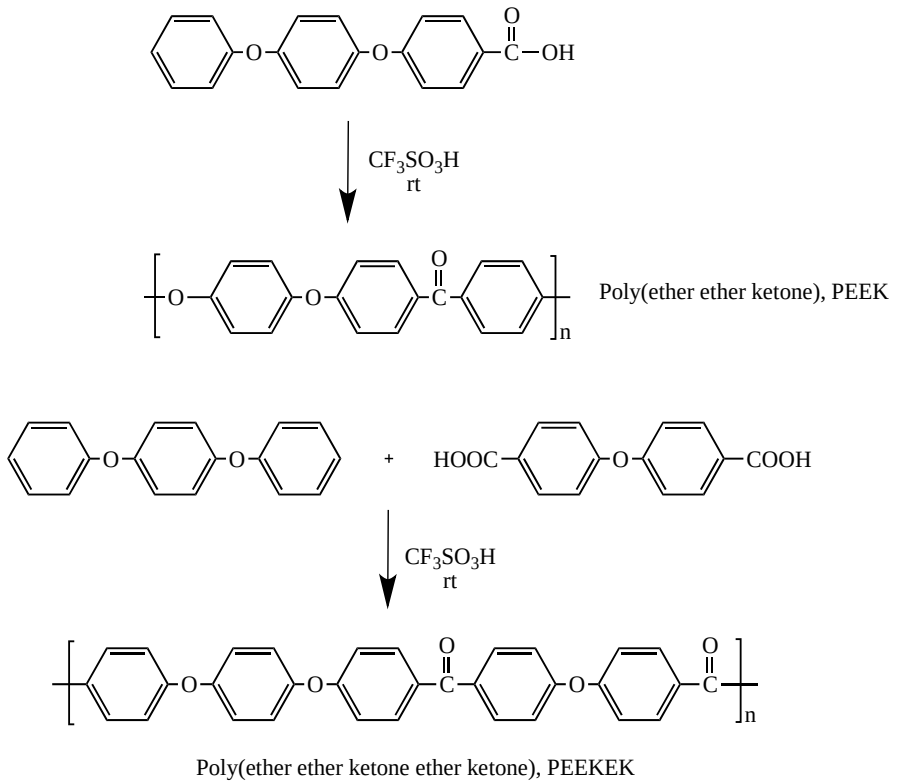
PAEK can be synthesized in two ways: electrophilic aromatic substitution (EAS) and nucleophilic aromatic substitution (NAS). In 1962, Bonner described the synthesis of completely aromatic poly(ether ketone). This synthesis was done by a Friedel-Crafts acylation reaction between diphenyl ether and terephthalyl chloride in the presence of nitrobenzene and aluminum chloride acts as a catalyst as shown in **Scheme 2**. However,

the polymer produced by this reaction had low molecular weight due to the insolubility in most organic solvents.[15]



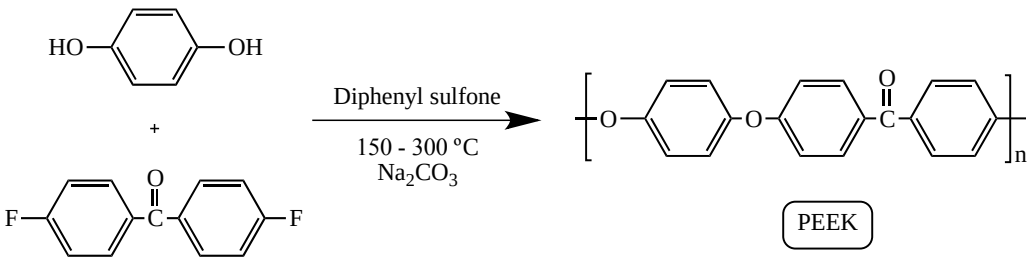
Scheme 2. Synthesis of poly(ether ketone ketone) by EAS.

PEK with higher molecular weight was synthesized by Marks using BF_3HF complex as a catalyst and liquid hydrogen fluoride as a solvent.[16] Later in 1983, Rose synthesized a high molecular weight PEEK using trifluoromethanesulfonic acid as a catalyst for the reaction of carboxylic acid with phenyl ether as shown in **Scheme 3.**[17]



Scheme 3. Synthesis of PEEK and PEEKEK by EAS

Due to the harsh reaction conditions and high costs, these syntheses did not find wide industrial application.[18] PEEK can also be synthesized by another common method, nucleophilic aromatic substitution using aromatic halides. Johnson, *et al.* synthesized the first PEEK, via NAS, by using bisphenol and 4,4'-difluorobenzophenone in the presence NaOH as base and DMSO as the solvent.[25] This synthesis produced low molecular weight PEEK because of solubility problems; polymer chains were precipitated during the reaction and the polymerization process stopped. The observed melting temperature (T_m) was 350° and the T_g around 160°. On further research, Attwood, *et al*. changed the solvent and base to diphenyl sulfone and Na_2CO_3 to obtain high molecular weight PEEK **(Scheme 4).**[19]



Scheme 4. Synthesis of poly (ether ether ketone) via NAS

1.1.3 Poly(arylene ether sulfone), PAES

Poly(arylene ether sulfone)s, PAES, are a class of amorphous polymers that are known as one of the most important members of the PAE family, in part due to the fact that they possesses excellent mechanical strength, as well as good resistance towards oxidation and hydrolysis. PAES possesses high glass transition temperature due to their rigid backbone composed of aromatic ether linkages, aryl and sulfone groups. The general structure of PAES is as represented in **Figure 4.**

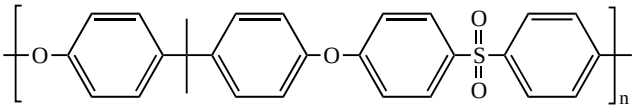
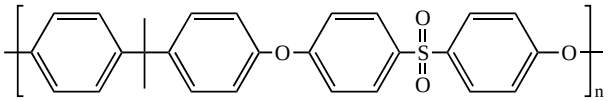


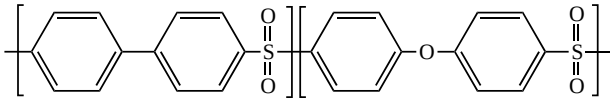
Figure 4. General structure of PAES

PAES also have poorer chemical resistance because of their less solubility in polar aprotic and halogenated solvents. However, PAES still have a wide range of industrial applications such as adhesives, films, membranes[20]connectors and composite materials. In 1965, Udel, the first commercial poly (arylene ether sulfone) was introduced by Union Carbide. Some of the major commercially available PAES are as shown in the **Figure 5.**[21] The relative high glass transition temperatures ranging from 190^o to 285^o is due to the

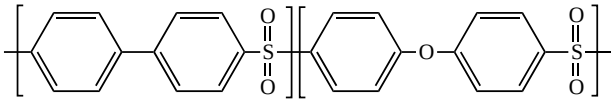
presence of rigid aromatic structures along with very polar sulfonyl groups and also due to varying bisphenol units.



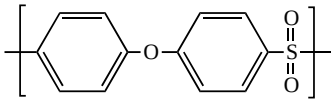
UDEL (Union Carbide) T_g = 190 ºC



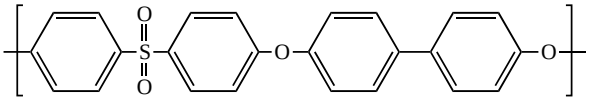
PES 720P (ICI) T_g = 250 ºC (b) Predominates



Astel (3M Corp) T_g = 285 ºC (a) Predominates



Victrex (ICI) T_g = 230 ºC

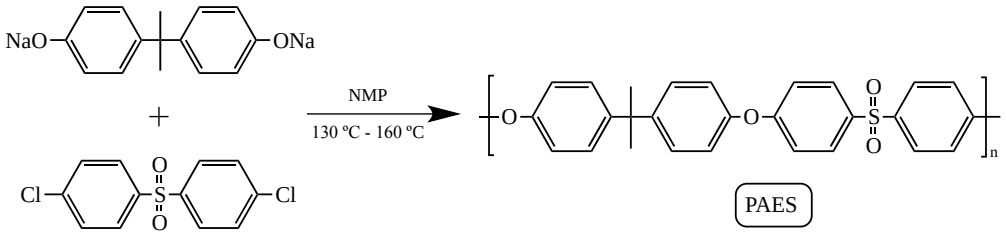


Radel (Union Carbide) T_g = 220 ºC

Figure 5. Commercially available PAES

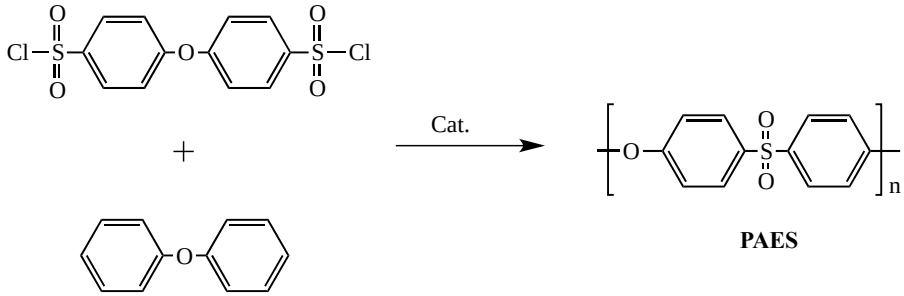
PAES can be synthesized by either an EAS or NAS polycondensation reaction.[22, 23]The commercial production of the thermoplastics is done by using the nucleophilic aromatic polycondensation. The first PAES synthesized by NAS was done by Johnson, *et al.* in 1960's. This synthesis involves two steps: conversion of Bisphenol-A into its

bisphenolate form and polycondensation with 4,4'-dichlorodiphenyl sulfone in aprotic solvents such as *N*-methyl-2-pyrrolidinone (NMP) or dimethyl sulfoxide (DMSO) **(Scheme 5)**.[2, 21]



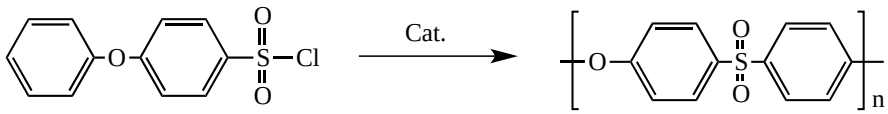
Scheme 5. Synthesis of poly (arylene ether sulfones), PAES by NAS

PAES can also be synthesized by EAS via polysulfonylation, in which aryl sulfonyl chlorides react with aromatic nucleophiles to form sulfone linkages as in **Scheme 6**. This synthesis involves three steps: reaction between the sulfonyl halide and Lewis acid resulting in the formation of sulfonylium ion, electrophilic addition and proton abstraction. PAES have been synthesized via EAS by reacting bis(4-chlorosulfonylphenylether) with diphenyl ether in the presence of a catalyst **(Scheme 6).**[21, 24]



Scheme 6. Synthesis of PAES by EAS

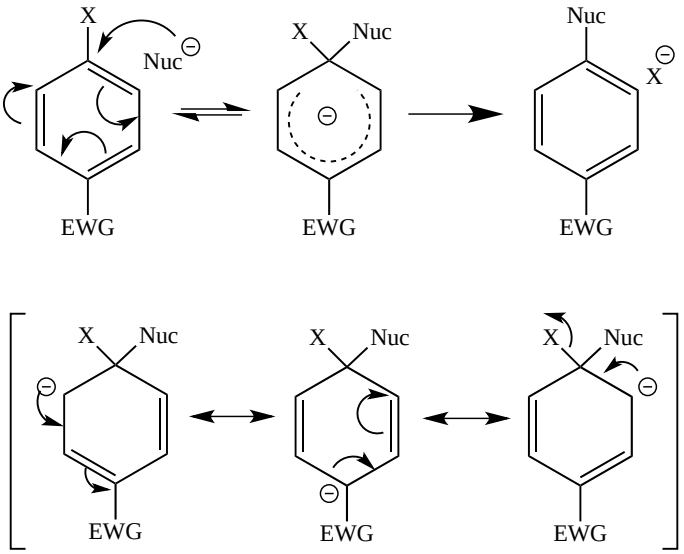
The backbone of PAES synthesized by this method are branched. In order to avoid branching, 4-chlorosulfonyldiphenylether, which is an AB monomer, was used **(Scheme 7).**[21]



Scheme 7. EAS of a single AB monomer route for PAES

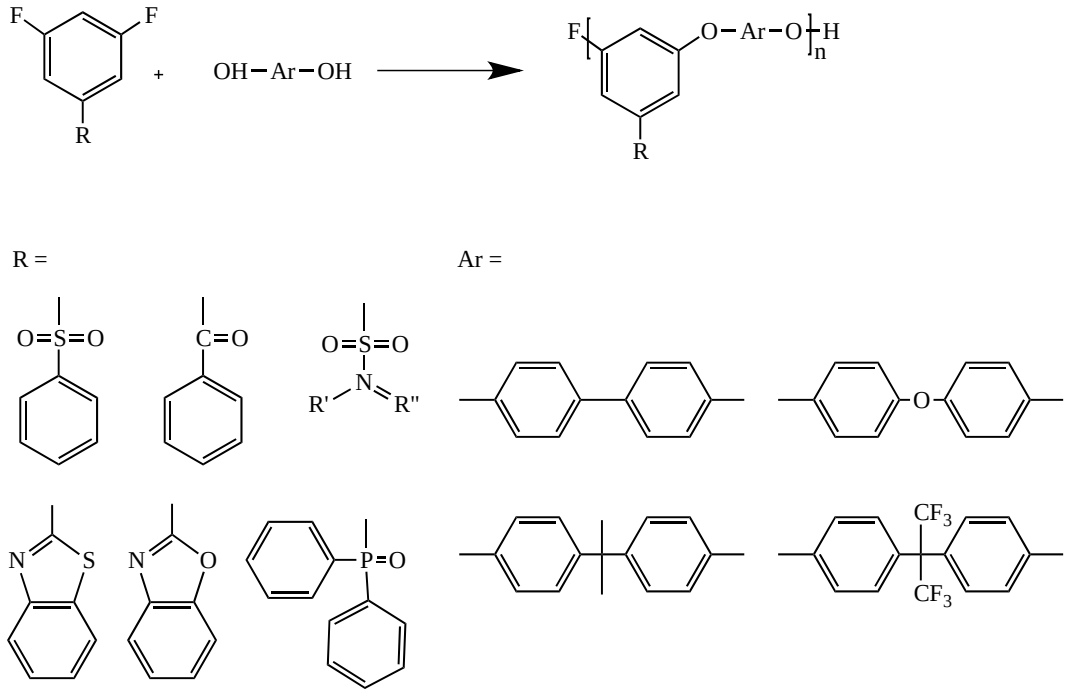
1.2 Synthesis of PAEs by Nucleophilic Aromatic Substitution

PAEs are commercially synthesized via the NAS pathway. NAS is a reaction that involves the substitution of an aryl halide by a nucleophile.[25, 26] The halide is activated for displacement by a strong electron withdrawing group (EWG) such as sulfonyl, carbonyl or phosphoryl group located either in the *ortho* or *para* position. As shown in **Scheme 8** the mechanism of a typical NAS reaction involves two steps: 1) addition of the nucleophile, 2) elimination of the leaving group**.**



Scheme 8. Typical NAS mechanism for a *para* activated system

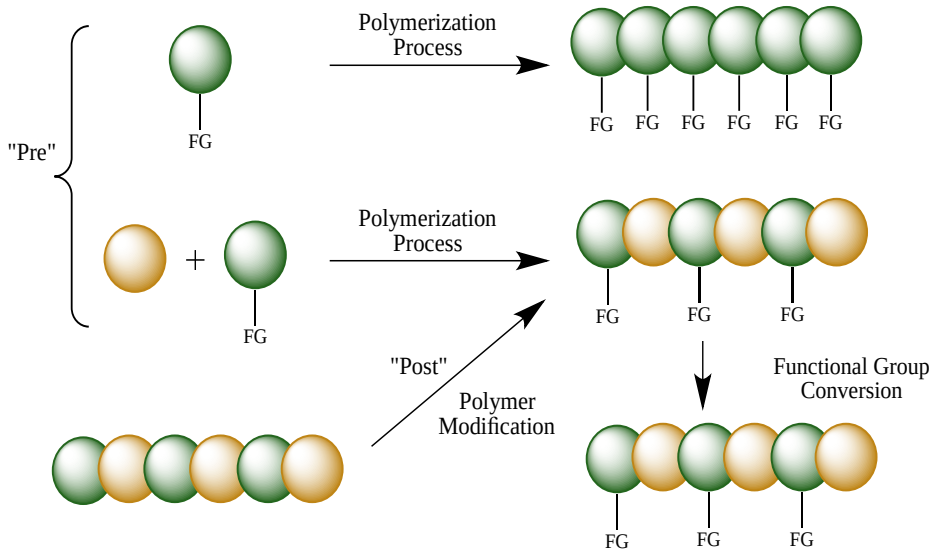
Usually, the first step is the rate-determining step and is reversible. In the first step, the attack of the nucleophile is at the *ipso* carbon resulting in the formation of the resonance stabilized intermediate carbanion known as a Meisenheimer complex. The EWG will activate the electrophilic site by decreasing the electron density at the *ipso* carbon and also helps to stabilize the Meisenheimer complex. This NAS mechanism was for the EWG at the *ortho* or *para* position but EWG at the *meta* position were also reported. The first *meta* activated NAS mechanism for the synthesis for 3,5-difluoro aromatic systems was studied by Kaiti, *et al*.[27a]These systems allow the activating groups to reside pendent to the polymer backbone and provide a chance to introduce functionality into the polymer, without altering the backbone structure of the polymer. Since then our group has synthesized several PAEs using *meta* activated NAS polycondensation reactions as shown in the **scheme 9**.[27a,27b, 27c,27d,27e,35



Scheme 9. Synthesis of PAE via *meta*- activated NAS polycondensation reactions

1.3 “Pre” and “Post” Modification Chemistry

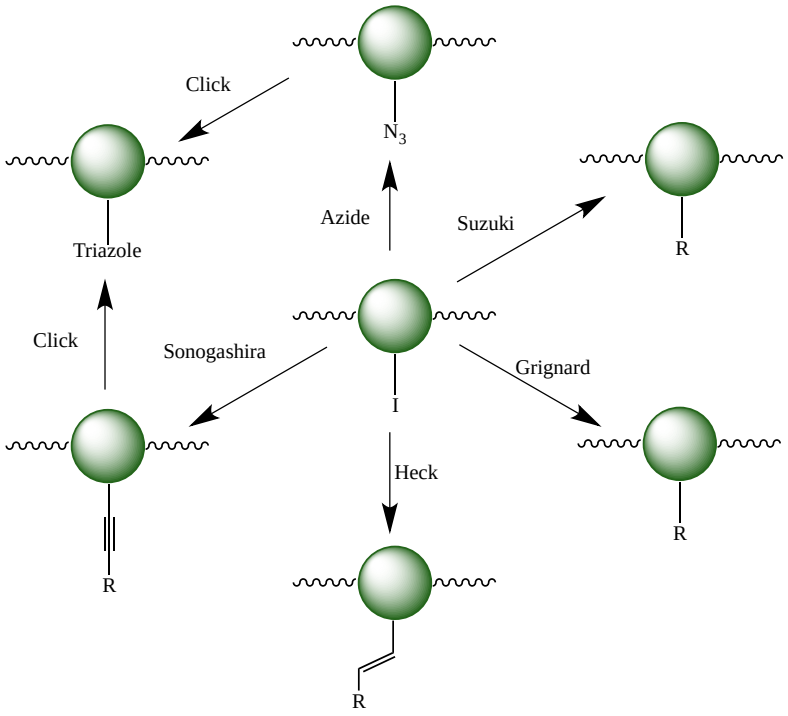
In order to meet the requirements of certain applications, polymer systems are modified by the introduction of functional groups to alter their physical and chemical properties. These modifications can be done in two ways: “pre” modification, done at the monomer stage, and “post” modification, done after the completion of polymerization. The scheme for the introduction of the functionality is as shown in **Scheme 10.** In “pre” modifications, the functionality is introduced at the monomer stage, followed by polymerization, whereas, in “post” modifications, the functionality is introduced at the polymer stage.



Scheme 10. Introducing functionality via “Pre” and “Post” modification chemistry.

Beside these, both the modifications have some advantages and disadvantages. The disadvantages of “pre” modification for the polymer systems involves multiple steps and also might lead to several undesired side reactions. In addition, the functional groups need to survive under the polymerization conditions. In order to avoid the side reactions, the

functional groups, which are not stable to NAS conditions, can be introduced at the polymer level. The functional groups, such as iodide introduced at the monomer level, will provide a site for further functionalization at the polymer level. Tatli, *et al*. from our group successfully demonstrated the "post" functionalization of iodo-containing aryl systems using Suzuki-Miyaura and Heck reactions. There are many possibilities for post modification reactions using aryl-iodide systems as shown in **Scheme 11**. However, the disadvantages of "post" modification, includes insufficient reactivity sites for the functional groups and also undesirable side reactions arising due to harsh modification conditions.[28]



Scheme 11. Post modification of aryl iodides.

1.4 Functionalization of PAEs

Introducing functional groups into the PAE systems was done before or after the polymer level in order to meet several applications of the high performance engineering materials.[29] Different functional groups such as sulfonic acids,[30] aldehydes,[31] alcohols,[31] amides,[31] ketones,[31] amines[32] and phosphoric acids[33] have been introduced into the PAE systems via "pre" and "post" modifications. In general, most of the functional groups were done in the *para* activated PAE systems, in which the group is attached directly onto the polymer backbone. In some of these systems, introduction of the functional group at the monomer level has being increasingly explored to prove that the polymers prepared by polycondensation reactions will have control over the quantity and location of functional groups. The functional groups that are introduced at the monomer stage must be able to withstand the polymerization conditions. As a result, all functional groups are not introduced at the monomer level. Some of them can be preferably introduced at the polymer stage.[34] The most common method used to introduce some functional groups onto the polymer backbone is post modification. The functional groups are either introduced on electron rich rings with electrophilic chemistry or on electron poor rings with anionic reactions as shown in **Figure 6.**[29] By this approach, the number of functionalized monomers that can survive the polymerization conditions[28] are reduced, but this will result in the significant changes in the polymer backbone. This will lead to the changes in the thermal and mechanical properties of these polymers.

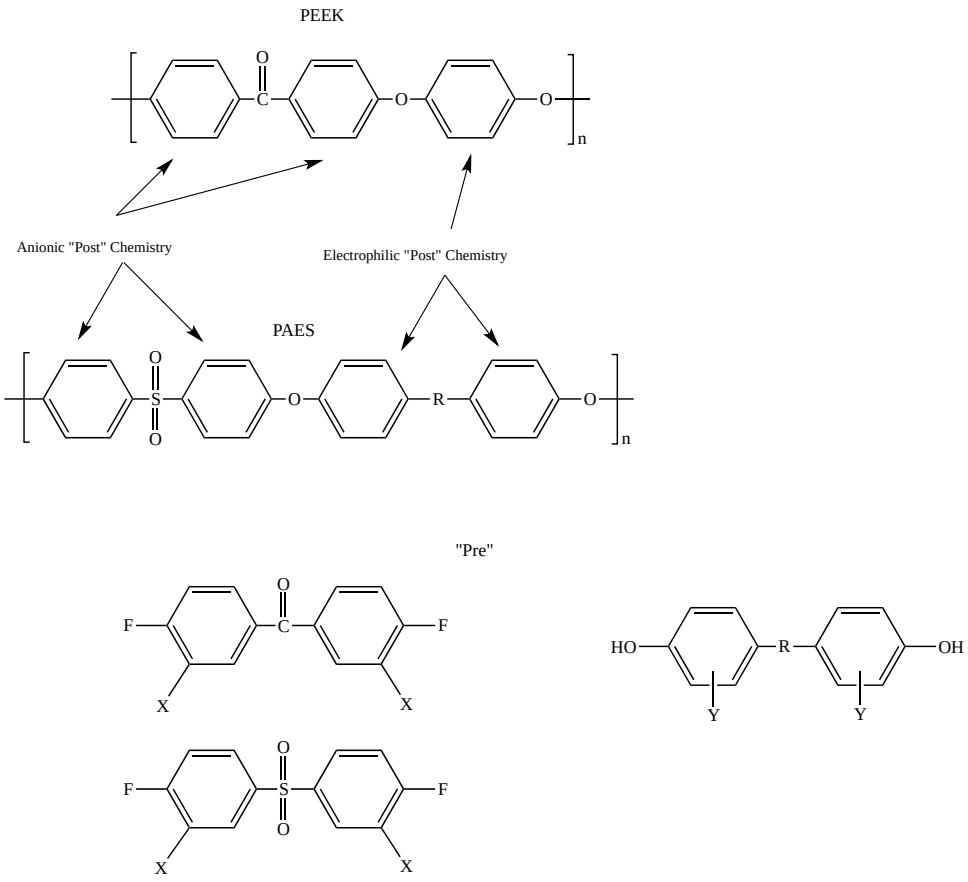


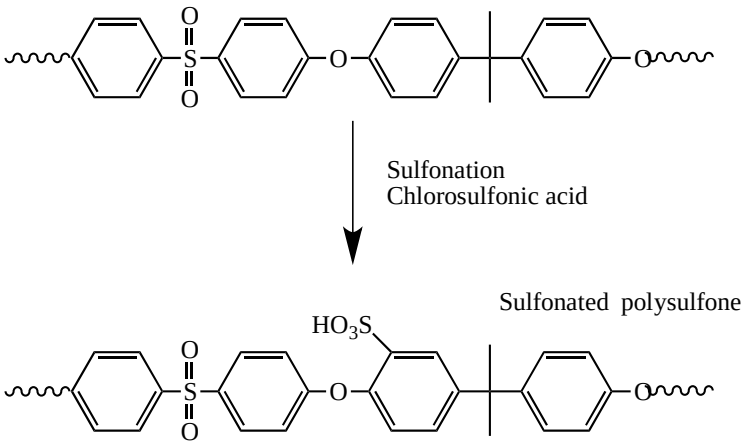
Figure 6. Routes to “pre” and “post” chemistry.

The recent development of *meta*-[27a, 27b, 27c, 34, 35]activated PAE systems have provided polymer chemists with a powerful tool for functionalization that can be done, via “pre” or “post” modification chemistry, to PAE systems without altering the polymer backbone. In these systems, the functional groups are located pendent to the polymer backbone, which will provide opportunities for further modification without altering the backbone structure.

1.4.1 Sulfonated PAES

Sulfonated PAES also have excellent mechanical and thermal properties similar to that PPO and PEEK. These properties will allow them to have several industrial

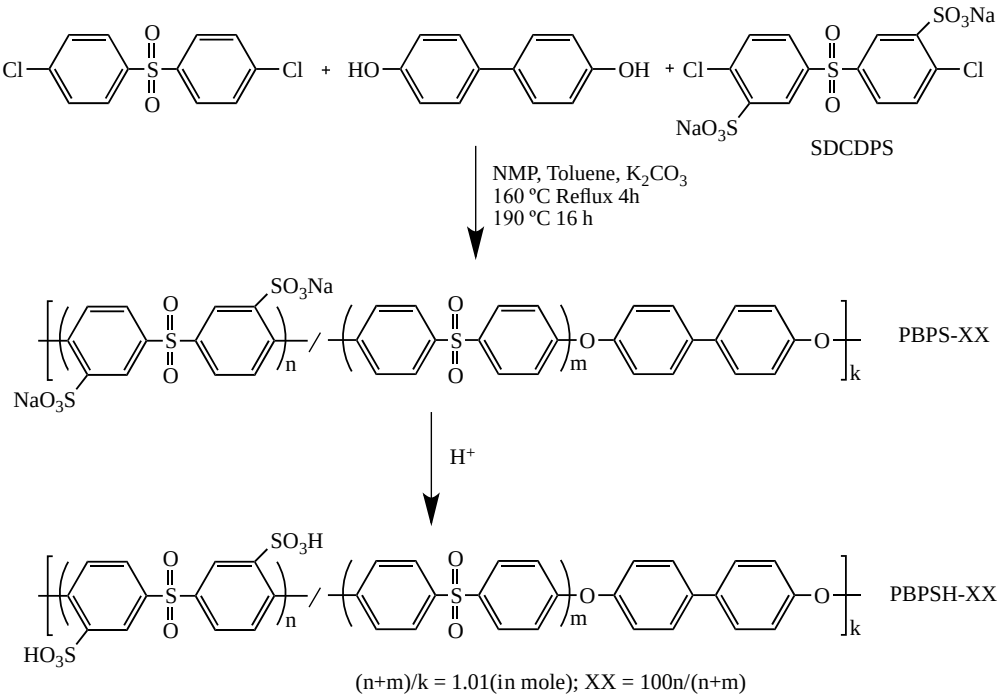
applications such as fuel cells[36] and reverse osmosis desalination processes.[37, 38] Quentin, *et al.* [39]was the first to use the sulfonation technique. Further research has been done in improving these techniques. The PAES can be effectively synthesized by two ways, "pre"-sulfonation of the monomer followed by the polymerization process[40] and "post"-sulfonation at the polymer level.[41] The synthesis of PAES, via "post" modification chemistry **(Scheme 12),** was studied by R.L. Orifice and A.Brennan.



Scheme 12. Sulfonation of PAES via "post" modification chemistry.

A new route to sulfonate PAES via "post" modification chemistry was introduced by Wang, *et al.* as shown in **Scheme 13.** In this synthesis, commercially available 4,4'-dichlorodiphenyl sulfone (DCDPS) and 4,4'-biphenol were used to synthesize the polymer. The ether group which is an electron donating group acts as *ortho* and *para* activator.[42]

According to Wang, *et al.*, "pre" sulfonation PAES has more advantages on the location as the sulfonic acid group is located in the *ortho* position to the ether linkage because the *para* position is blocked and sulfonation levels are also readily controlled.[43, 44]



Scheme 13. Synthesis of sulfonated PAES via "pre" modification.

After the "pre" modification, the sulfonate groups are located in the *meta* position, since the sulfonyl group is a *meta*- director. According to Wang, *et al.* two sulfonyl groups (possible only via "pre" modification) present on the electron poor ring will increase the acidity and stability of the polymer.[45]

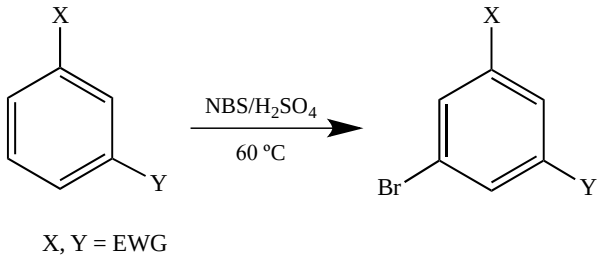
Applications of sulfonated PAES in fuel cell applications and desalination process are similar to that of sulfonated PEEK and PPO. Ongoing research on fuel cells has shown that the sulfonated PAES has gain more attention as it shows similar results to Nafion®, that has high proton conductivity and chemical stability than other sulfonated PAE.[46,47]Park, *et al*. combined a progression of disulfonated PAES arbitrary copolymers with different proportions of sulfonated sulfonyl monomer and non-sulfonated sulfonyl or phosphoryl monomer to screen the water penetrability and salt dismissal in saline membranes.[38] They reasoned that the fresh water will experience the increase in membrane

with the increase in sulfonated monomer level. However, the salt dismissal (salt that is kept by the membrane) diminishes. Then again, at the point when more amount of the polar monomer unit (phosphoryl monomer) is utilized, the outcomes acquired are *vice versa* to the fact that the more polar gathering interacts with SO_3H through H-holding.[38] The sulfonated systems are utilized in desalination and fuel cell applications.

1.4.2 Halogenated PAE

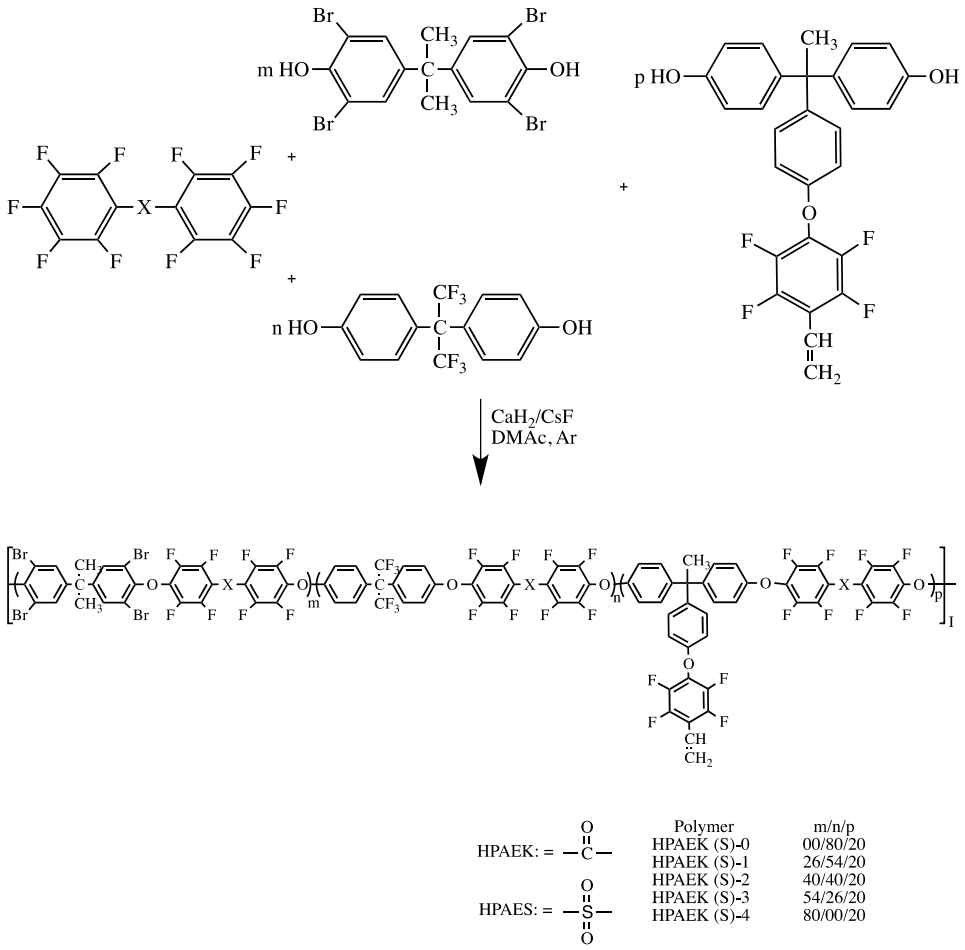
Another example of functionalization is to introduce halogens into the PAE systems at the monomer level. There are a few approaches to halogenate PAE systems such as electrophilic halogenation, free radical halogenation,[48] ketone halogenations and halogen addition.[48] In general, PAE systems undergo electrophilic aromatic substitution (EAS), saturated hydrocarbons incline toward free radical halogenations, while alkenes and alkynes experience addition reactions.[48]

EAS with *N*-Bromosuccinimide (NBS) or *N*-Iodosuccinimide (NIS) is a successful approach to functionalize aryl compounds. Rajesh, *et al*. studied a series of bromination reactions using NBS and H_2SO_4 of deactivated aromatic compounds as in **Scheme 14**.[49] These reactions are done using concentrated sulfuric acid at 60^o and the yields obtained were 80-90%. Electron withdrawing groups such as CHO, COOH, NO_2 and CN, are all *meta* directors and direct the bromine group to the *meta* position on the ring.



Scheme 14. Bromination via NBS.

In 2004, Prakash, *et al*. studied a new synthetic route for the halogenation of deactivated aromatic compounds by using H_2SO_4 instead of BF_3-H_2O and *N*-halosuccinimides in the temperature ranging from 0º-105º. Different isomers such as *ortho, meta and para* isomers are obtained[50] depending on the activating group on the aromatic compounds. Functional groups such as iodine and bromine are introduced into PAE by modifying the target monomer followed by polymerization. Qi, *et al.*[51]have synthesized PAEK and PAES with different ratios of bromine by incorporating it into the bisphenol component (**Scheme 15**). These halogenated PAE have been used as waveguide materials.

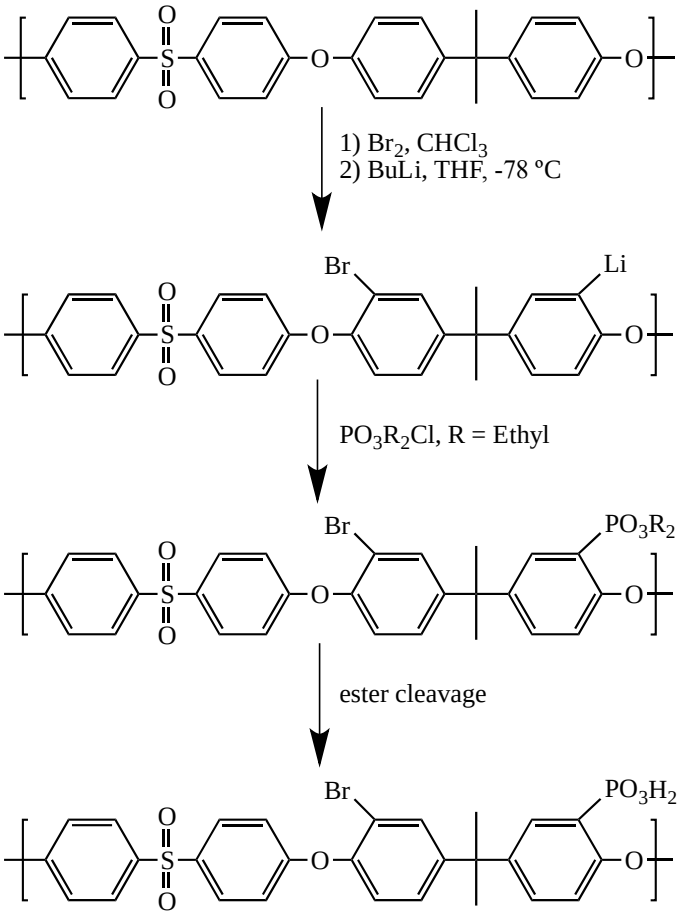


Scheme 15. Synthesis of halogen-rich PAEK and PAES.

It was concluded that the polymers containing more C-Br bonds have a superior tuning of the refractive index, which is a vital parameter for waveguide materials. Therefore, by changing the brominated monomer proportion, the refractive index could be effectively tuned.

Phosphonation of PAE can also be done at the "post" stage (polymer level). Lithium- halogen exchange reaction followed by phosphonation as shown in **Scheme 16**,[33]as an example for "post" halogenation. The objective was to obtain a polyelectrolyte

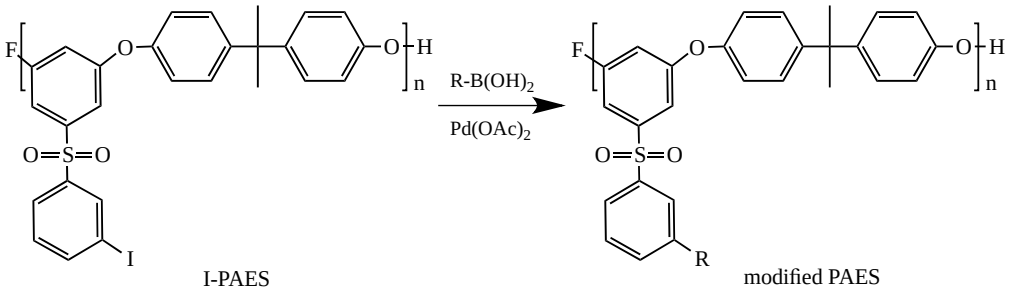
poly-sulfone that can be used in fuel cells and also increase the applications of the polymers by introducing bromine groups[33] for further functionalization.



Scheme 16. Bromination and Lithiation of a poly (sulfone)

Tatli, *et al.*, studied the synthesis of **PAES**, with a pendent aryl iodide via *meta* activated NAS polycondensation of a 3,5-difluoro-aromatic monomer. These monomer systems provide a powerful tool for introducing functionality into PAE systems. Polymerization was done to these iodo monomer systems using Bisphenol-A in the presence of K_2CO_3 and NMP to obtain iodo functionalized polymers. Post modification was done to the iodo polymer via a Heck cross-coupling reaction with styrene and Suzuki-Miyaura cross-coupling reactions with phenyl, naphthyl and phenyl acetyl boronic acids as

shown in **Scheme 17**.[34] Using this modification, a series of PAES with different pendent groups were obtained. These polymers exhibited thermal stability above 400^{o} with a T_g values ranging from 131^{o} to 165^{o}.[34]



I-PAES modified PAES

Scheme 17. Example of post modification of aryl iodides.

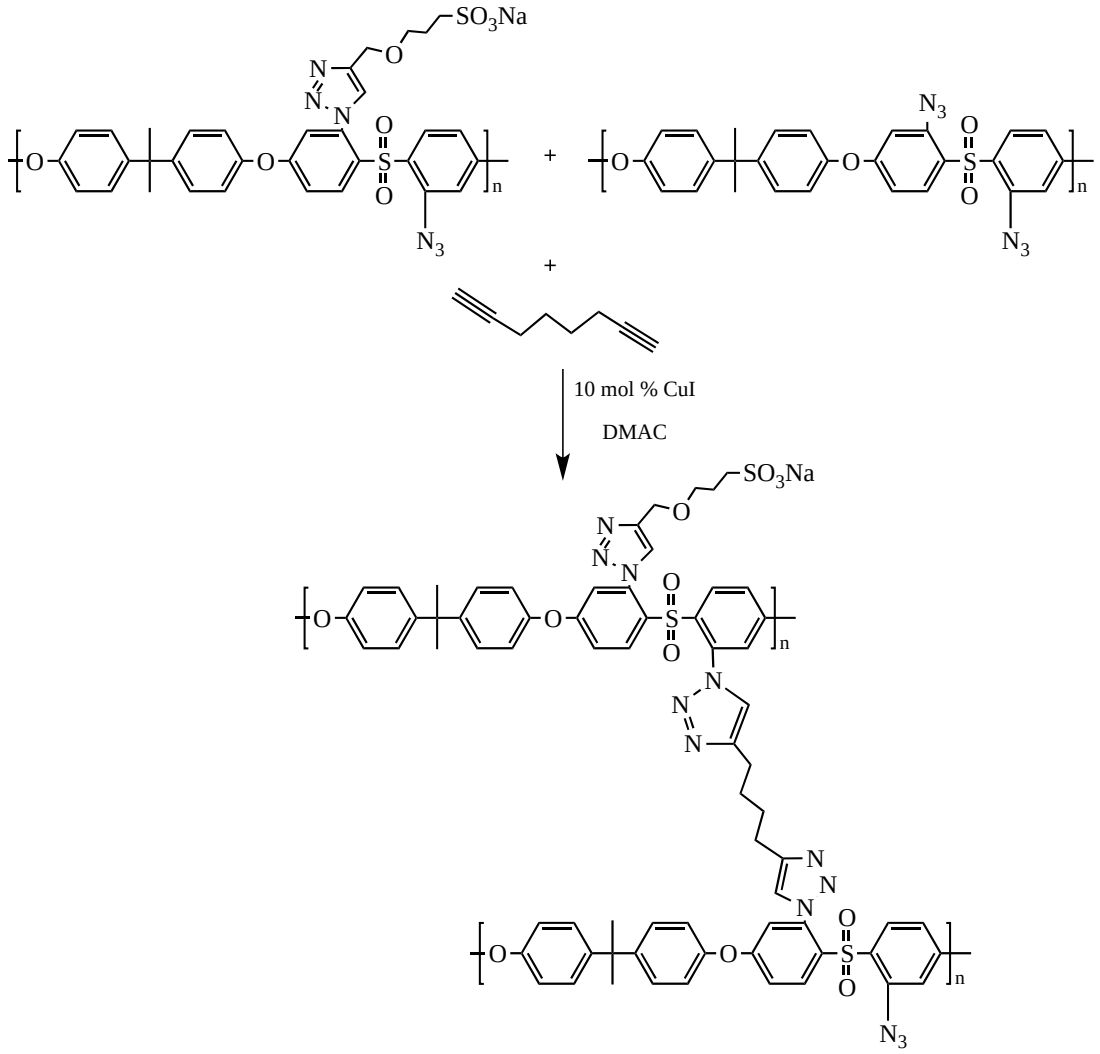
1.4.3 Click Chemistry

In 2001, K.B. Sharpless has introduced the term "Click Chemistry" to describe reactions that produce high yield, are wide in scope, form only byproducts that can be easily removed using chromatography, are stereospecific, and are simple to perform in easily removable solvents. One of the most effective and well-known click reactions is the cycloaddition of azide and alkynes, the Huisgen 1,3-dipolar cycloaddition,[52a, 52b] which yields a 1,2,3-triazole. In 2001, Kolbe,*et al.*[53]was the first group to explore on the 1,3-dipolar cycloaddition reaction.

Though it was explored fully still there are some disadvantages such as the formation of regioiosmers to this cycloaddition reaction. To overcome this, in 2002, Sharpless and his co-workers studied and introduced a new approach leads to the formation of a 1,2,3- triazoles using the Cu-catalyzed Huisgen cycloaddition reaction between non-activated alkynes and alkyl/aryl halides[54a] under a variety of reaction conditions. This is

most uncommon reaction in organic synthesis, in which the azides and alkynes can be introduced into the molecules under certain reaction conditions. Azides and alkynes are introduced in most of the highly functional organic molecules. The Sharpless "click" reaction has several advantages such as allowing functional group variability, solubility in common organic solvents, use of different interfaces like liquid-liquid, solid-liquid, etc, simple workup, easy purification procedures and high yields.

Click chemistry has wide applications in combinatorial chemistry, organic synthesis, bio conjugation, drug discovery, nanotechnology, materials and polymer sciences. In polymer chemistry, the functionalization of the polymer via click chemistry is done at the "post" stage. Click chemistry also has several applications in the material science such as block, star, graft, dendritic architectures and also in polymeric networks having azide/alkyne functional groups in the sidechains. Click chemistry also has industrial applications such as fuel cells. Norris, *et al*. synthesized crosslinked azide polysulfone copolymer membrane via click chemistry using *n*-butyl lithium, *p*-toluenesulfonyl azide, partially sulfonated polysulfone and 1,7-octadyne as shown in **Scheme 18**.[55] In this,1,7-octadyne acts as a crosslinker to improve the conductivity and performance of fuel cell membranes.



Scheme 18. Synthesis of sulfonated poly (sulfone) copolymer via crosslinking.

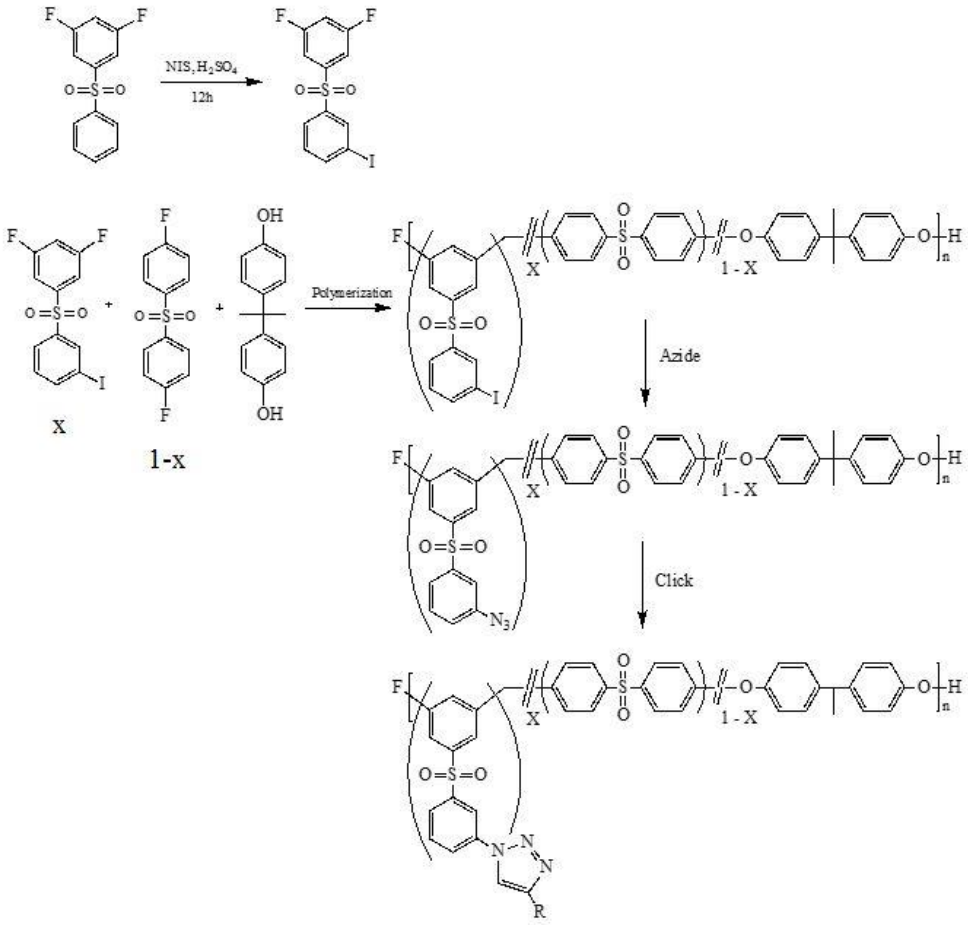
1.5 Current work

This project consists of two parts. In the first part, 3,5-difluorodiphenylsulfone acts as starting material and also a monomer was synthesized. The structure of 3, 5-difluorodiphenylsulfone contains two aromatic rings, in which one aromatic ring will contain two fluorine atoms in the *meta* positions, relative to the sulfone, while the other aromatic rings remains unsubstituted and provides a site for introducing functional groups, either via the "pre" or a combination of the "pre" and "post" methodologies.

The introduction of the iodide functional group is done via electrophilic aromatic substitution (EAS) reaction at "pre" stage. In this synthesis, electrophilic aromatic substitution reaction is expected to occur on the non-fluorinated ring, as the sulfone is a strong *meta* director. This will provide a site for further functionalization as it shows very low reactivity in NAS reactions.[27a]

Once the iodination is done, polymerization of the iodinated monomer is done using 4,4'-difluorodiphenyl sulfone and Bisphenol-A with a ratio 25:75:100 as shown in **Scheme 19.** This polymer was fully characterized before subjecting it to further functionalization.

The second part of the project is the post functionalization of the iodinated copolymer with azide functional group. The iodinated copolymer is functionalized at the polymer level will be subjected to copper catalyzed C-N bond forming azide modification reaction using sodium azide as shown in **Scheme 19**. Azide copolymer is characterized and then further functionalized using click chemistry with different alkynes as shown in **Scheme 19.**



Scheme 19. Synthetic route for triazoles via click chemistry.

2. EXPERIMENTAL

2.1 Instrumentation

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired using a Bruker AVANCE 300 MHz instrument operating at 300, and 75.5 MHz, respectively. Samples were dissolved in $CDCl_3$ at a concentration of (~ 30 mg/ 0.7 mL). GC/MS analyses were performed using an Agilent Technologies 7820A Series GC System and an Agilent Technologies 5975 Mass Selective Detector/Quadrupole system. DSC and TGA analysis were carried out on TA Instruments DSC Q200 (under nitrogen) and TGA Q500 (under nitrogen or air), respectively, at a heating rate of 10^{o}/min. Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Two Polymer Laboratories 5 µm PL gel Mixed C columns (heated to 35^{o}) were used with 95% (v/v) tetrahydrofuran/ 5% (v/v) glacial acetic acid as the eluent and a GPC max VE-2001 with pump operating at 1.0mL/min. Weight average molecular weights, M_w, Number average molecular weight, M_n and Dispersity were determined using OmniSec software (calibrated with polystyrene standards). Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector.

2.2 Materials

3,5-difluorodiphenylsulfone **1** was synthesized using the previously reported route.[27a] *N*-iodosuccinimide (NIS) was purchased from Acros Organics and used as received. *N*-methylpyrrolidinone (NMP) was purchased from Sigma Aldrich Chemicals Co. and was dried over CaH_2 and distilled under nitrogen prior to use. Chloroform ($CHCl_3$),

fuming sulfuric acid (H_2SO_4) and toluene were purchased from VWR and used as received. Tetrahydrofuran (THF), Dichloromethane (DCM) and isopropyl alcohol (IPA) were used as received from Avantor. Bisphenol A and 4,4'-Difluorodiphenylsulfone were purchased from Sigma Aldrich Chemicals Co., recrystallized from toluene and dried *in vacuo* prior to use. Reagent-grade anhydrous potassium carbonate powder (K_2CO_3) was purchased from Sigma Aldrich Chemicals Co., and dried at 130° in an oven prior to use. ACS certified acetone was used as received from Macron and ethanol from Decon Laboratories. Sodium bicarbonate ($NaHCO_3$), magnesium sulfate ($MgSO_4$) and methanol were used as received from Fischer Scientific. Deuterated chloroform ($CDCl_3$-d_6) was purchased from Sigma Aldrich and used as received. Anhydrous copper sulfate ($CuSO_4$) was purchased from Baker and used as received. (+) Sodium L-ascorbate, phenyl acetylene, 1-octyne were used as received from Sigma Aldrich Chemicals Co. Sodium azide was purchased from Fischer Scientific and used as received.

2.3 Synthesis of 1-(3, 5-Difluorophenylsulfonyl)-4-iodobenzene 2:

In a 50 mL RB flask, equipped with a stir bar, were placed 3,5-difluorodiphenyl sulfone **1** (2.5 g, 9.8 mmol) and concentrated H_2SO_4 (12.3 mL). To the vigorously stirred solution *N*-iodosuccinimide (NIS) (2.2 g, 14.3 mmol) was added slowly and the resulting mixture was allowed to react at room temperature for 12 h. After 12 h, the reaction mixture was slowly poured into a large excess of water and the resulting solid was isolated via filtration. The solid was redissolved in approximately 50 mL of dichloromethane and then washed with a dilute sodium bisulfite solution. The organic layer was dried over $MgSO_4$ and the solvents were removed via rotary evaporation resulting in a yellowish product (3.0 g). The crude product was recrystallized from isopropanol to afford off white crystals 1.9

g (52%) of **2** with a melting point of 158-159^{o}. ^{1}H NMR ($CDCl_3$,δ): 7.05 (tt, 1H), 7.28 (t, 1H), 7.48 (m, 2H), 7.91 (ddd, 1H), 8.27 (t, 1H). ^{13}C NMR ($CDCl_3$, δ): 94.8 (Ar_{C-I}), 109.4, 111.4, 127, 131, 136.4 , 142.0, 144.3, 162.9.

2.4 Polymerization of Iodo monomer 2 to Iodo copolymer (25%) 3:

The iodo monomer, 3,5-DFDPS-I **2** (1.2 g, 3.2 mmol), 4, 4'-difluorodiphenyl sulfone (4,4'-DFDPS) (2.4 g, 9.5 mmol) and Bisphenol-A (2.80 g, 12.6 mmol) were added in the ratio of 25:75:100, respectively, into a 100mL RB flask equipped with a stir bar, condenser and nitrogen inlet. To this flask, NMP (19.6 mL) and potassium carbonate (K_2CO_3) (3.5 g, 25.2 mmol) were added. Then the reaction flask was immersed in oil bath and stirred vigorously at 150^{o} for 24h. After 24 h was done, the reaction mixture was allowed to cool to room temperature and precipitated by adding slowly into vigorously stirring DI water. The resulting grey solid was isolated by vacuum filtration. The solid was dissolved in THF and reprecipitated from ethanol, filtered and dried to afford 3.2 g (76%) of **3** as an off-white solid. ^{1}H NMR ($CDCl_3$, δ): 1.69 (s, 6H), 6.81 (t, 3H), 6.91 (d, 4H), 7.0 (d, 2H), 7.19 (d, 2H), 7.24 (d, 4H), 7.62 (d, 4H), 7.83 (bd, 1H) ,7.87 (bd, 1H),7.90 (d, 2H), 8.15 (b, 1H). ^{13}C NMR ($CDCl_3$, δ): 30.9, 42.4, 95.1(Ar_{C-I}), 110.9,112.5, 117.7, 119.1, 119.8, 128.4, 129.7, 135.4, 136.2, 142.3, 146.9, 147.1, 152.8, 153.1, 159.7, 161.9.

2.5 Synthesis of Azide Copolymer 4:

The Iodo copolymer **3** (1.00 g, 2.0 mmol), sodium azide (0.27 g, 4.1 mmol), sodium ascorbate (0.82 g, 0.4 mmol) and *N, N*-dimethylethylenediamine (33.7 µL, 0.3 mmol) were added into a 100 mL Schlenck flask, equipped with nitrogen inlet and a stir bar. The reaction mixture was allowed to stir at room temperature. The entire setup was flushed with

nitrogen before the addition of NMP (2.9 mL) and water (3.7 µL). Then the polymer was allowed to dissolve at rt under N_2 atmosphere. Once the polymer was completely dissolved, first freeze pump thaw was performed. Then the entire setup was again flushed with nitrogen followed by the addition of copper sulfate (0.08 g, 0.3 mmol) and water (3.7 µL, 0.2 mmol). A second freeze pump thaw was performed. Then the reaction mixture was allowed to stir and react at room temperature for 48 h. Then the reaction mixture was precipitated from vigorously stirring DI water and the solid was obtained via vacuum filtration, allowed to dry under vacuum. Finally, yellow solid of copolymer **4** with yield (52%) was produced. ^{1}H NMR ($CDCl_3$, δ): 1.72 (s, 6H), 6.82 (t, 1H), 6.94 (d, 4H), 7.23 (m, 7H), 7.50 (m, 3H), 7.61 (t, 1H),7.85 (dd, 2H), 7.96 (dd, 2H) . ^{13}C NMR ($CDCl_3$,δ): 30.9, 42.4, 110.9, 117.6, 118.0, 119.1, 119.4, 119.8, 123.9, 128.4, 129.7, 130.8, 135.4, 141.9, 147.1, 152.8, 153.1, 159.7, 161.9. IR (KBr) 2108 cm^{-1} (aryl azide stretch)

2.6 General procedure for Post modification of 4 into Triazole Copolymers 5a-d using Click Chemistry:

A slightly modified version of Cu-catalyzed cycloaddition reaction first reported by Sharpless was used for click reactions. A post modification reaction for azide copolymer was described using click chemistry. As a representative example for triazole synthesis using 1-octyne **5a**: to a 25 mL Schlenck flask equipped with a magnetic stir bar, nitrogen inlet, azide copolymer **4** (250 mg, 0.5 mmol), sodium ascorbate (26 mg, 0.1 mmol) and *N*,*N*-dimethylethylenediamine (8.4 µL, 0.07 mmol), 1-octyne (10.8 µL, 0.5 mmol) were added. The entire setup was flushed with nitrogen followed by the addition of NMP (0.7 mL) and water (0.9 µL) and stirred until the entire polymer was dissolved. The first freeze pump thaw was performed after the polymer was completely dissolved. Then copper

sulfate (19 mg, 0.07 mmol) was added followed by the addition of water (0.9 µL).The entire set was again flushed with nitrogen and a second freeze pump thaw was performed. The reaction mixture was allowed to stir for 30 min at rt. Then the reaction mixture was heated in oil bath at 60^{o} and left to react for 12 h. Then the reaction mixture was precipitated from vigorously stirred DI water, solid was filtered and dried under vacuum to obtain a yellow solid (160 mg, 58%). ^{1}H NMR ($CDCl_3$, δ): 0.81 (dd, 3H), 1.27 (m, 8H), 1.69 (s, 6H), 2.3 (dd, 2H), 6.81 (t, 3H), 6.91 (d, 4H), 7.0 (d, 2H), 7.19 (d, 2H), 7.24 (d, 4H), 7.62 (d, 4H), 7.83 (bd, 1H) ,7.87 (bd, 1H),7.90 (d, 2H), 8.18 (b, 1H), 8.2 (b, 1H). ^{13}C NMR ($CDCl_3$,δ): 14.0, 18.4, 22.5, 28.4, 28.9, 29.2, 30.9, 31.3, 31.5, 42.4, 111.0, 117.6, 118.7, 119.1, 119.5, 119.8, 124.8, 127.1, 128.4, 129.7, 130.9, 135.4, 146.9, 147.1, 152.8, 153.1, 153.3, 159.7, 161.9.

5b using phenyl acetylene: yellow solid (153 mg, 55%). ^{1}H NMR ($CDCl_3$,δ): 1.62 (s, 6H), 6.79 (t, 3H), 6.94 (d, 4H), 7.0 (d, 2H), 7.09 (d, 2H), 7.2 (d, 4H),7.39 (dd, 1H), 7.45 (dd, 2H), 7.58 (dd, 2H), 7.62 (d, 4H), 7.83 (bd, 1H) ,7.87 (bd, 1H),7.96 (d, 2H), 8.15 (b, 1H), 8.35 (b, 1H) ^{13}C NMR ($CDCl_3$,δ): 30.9, 42.4, 111.0, 116.2, 117.6, 119.1, 119.8, 121.7, 125.9, 128.4, 129.6, 132.1, 132.4, 135.4, 147.1, 152.8, 159.8, 161.9.

5c using propargyl alcohol: Light green solid (110 mg, 51%). ^{1}H NMR ($CDCl_3$,δ): 1.65 (s, 6H), 1.81 (s, 1H), 4.38 (s, 1H), 6.81 (t, 3H), 6.91 (d, 4H), 7.0 (d, 2H), 7.19 (d, 2H), 7.24 (d, 4H), 7.45 (s, 1H), 7.62 (d, 4H), 7.83 (bd, 1H) ,7.87 (bd, 1H),7.96 (d, 2H). ^{13}C NMR ($CDCl_3$,δ): 30.9, 42.4, 58.4, 111.0, 117.6, 119.0, 119.4, 119.8, 128.4, 129.7, 135.4, 146.7, 147.1, 152.8, 153.3, 159.3, 161.9.

5d using acetylenedicarboxylic acid: Reddish brown solid (148 mg, 72%). ^{1}H NMR ($CDCl_3$,δ): 1.62 (s, 6H), 1.82 (bs, 2H), 6.80 (t, 3H), 6.91 (d, 4H), 7.0 (d, 2H), 7.19 (d, 2H), 7.24 (d, 4H), 7.63 (d, 4H), 7.85 (bd, 1H) ,7.87 (bd, 1H),7.95 (d, 2H). ^{13}C NMR ($CDCl_3$,δ): 30.6, 30.9, 42.4, 111.0, 117.6, 119.0, 119.4, 119.8, 128.0, 128.4, 129.7, 130.1, 135.4, 146.7, 147.1, 152.8, 153.3, 159.3, 161.9, 172.3.

2.7 CHARACTERIZATION:

2.7.1. Thermogravimetric Analysis (TGA):

The thermal stability of the polymers was analyzed using a TA Instruments Q500 Thermogravimetric Analyzer. The analysis was done by heating 5 mg sample, at a rate of 10^{o}/min, from 40^{o} to 800^{o} under nitrogen or air atmosphere. The weight loss was reported as $T_{d5\%}$ weight loss which is recorded as a function of temperature and thermal stability.

2.7.2. Differential Scanning Calorimetry (DSC):

The thermal transition temperatures were determined by using a TA Instruments Q200 Differential Scanning Calorimeter. A typical method involves heating 3-10 mg of sample in T_{zero} aluminum pan, at 10^{o}/min from 40^{o} to 350^{o} and cooling at 10^{o}/min to 40^{o} in two cycles under a nitrogen atmosphere. The glass transition temperature (T_g) was determined at the midpoint of the tangent of the second heating cycle. The first heating cycle was utilized to eliminate the thermal history of the polymers.

2.7.3. Size Exclusion Chromatography (SEC):

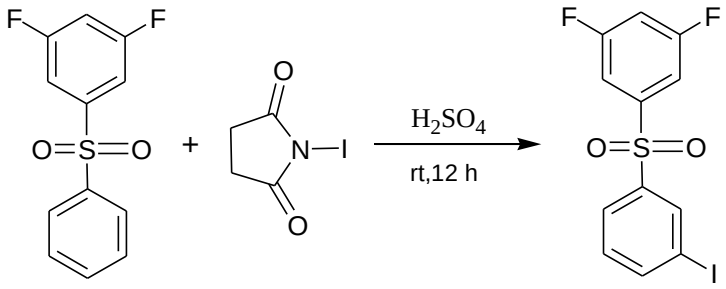
The molecular weight and molecular weight distributions of polymers were determined by using Size Exclusion Chromatography. Number average molecular weights

(M_n), and polydispersity index (PDI) were determined to the polymers soluble in THF/5% acetic acid using refractive index (RI) signals. Weight average molecular weights (M_w) were determined by using the light scattering signal. Polystyrene standards were used for calibration.

3. RESULTS & DISCUSSION

3.1 Synthesis of 1-(3, 5-Difluorophenylsulfonyl)-4-Iodobenzene 2

The first monomer, 3,5-difluorodiphenylsulfone **1**, was synthesized using the previously established procedure by Kaiti, *et al.*[27a] The iodination of the monomer **1** was carried out via typical electrophilic aromatic substitution using a slight excess of NIS as shown in (**Scheme 20**). From ^{13}C NMR data, it can be seen that the furthest upfield chemical shift of the carbon atom, located between the two fluorine atoms on the upper flourinated ring of the monomer as shown in **Scheme 20**. As this site being the most electron rich, the iodination is expected to take place on the upper ring but it is observed to take place on the bottom unfluorinated ring in the *meta*-position relative to the sulfone group. The steric effect of the two fluorine atoms in the upper ring prevents the electrophilic aromatic substitution of the iodide group on the upper ring instead it forces the iodide group onto the bottom ring which is more suitable reaction site for further substitution.



1 **2**

Scheme 20. Synthesis of **2** via Electrophilic Aromatic Substitution.

After the completion of the reaction, GC/MS analysis of the crude product showed approximately 99% conversion to mono-iodinated product and approximately 1% di-iodinated product. The reaction mixture was slowly poured into excess DI water and the

resulting solid was isolated by filtration. The crude product was subjected to a workup procedure, which included dissolving in dichloromethane washing with 5% sodium bisulfite solution to remove excess free iodide and recrystallization twice from isopropanol, after which off-white crystals (52%) were obtained with a melting point of 158-159^{o}. The monomer structure was confirmed by GC/MS analysis, as well as ^{1}H and ^{13}C NMR spectra as shown in **Figures 7 and 8**, respectively.

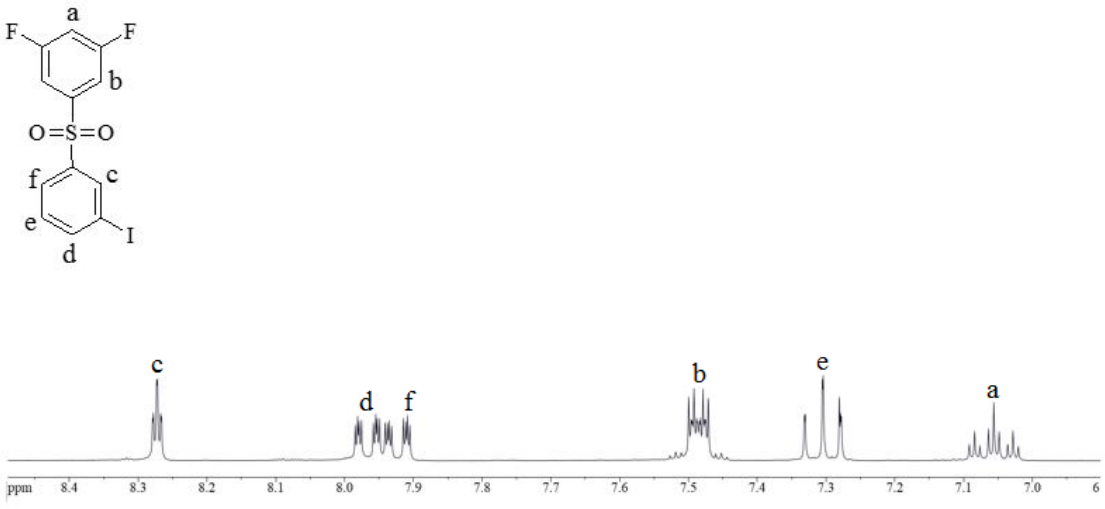


Figure 7. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **2**.

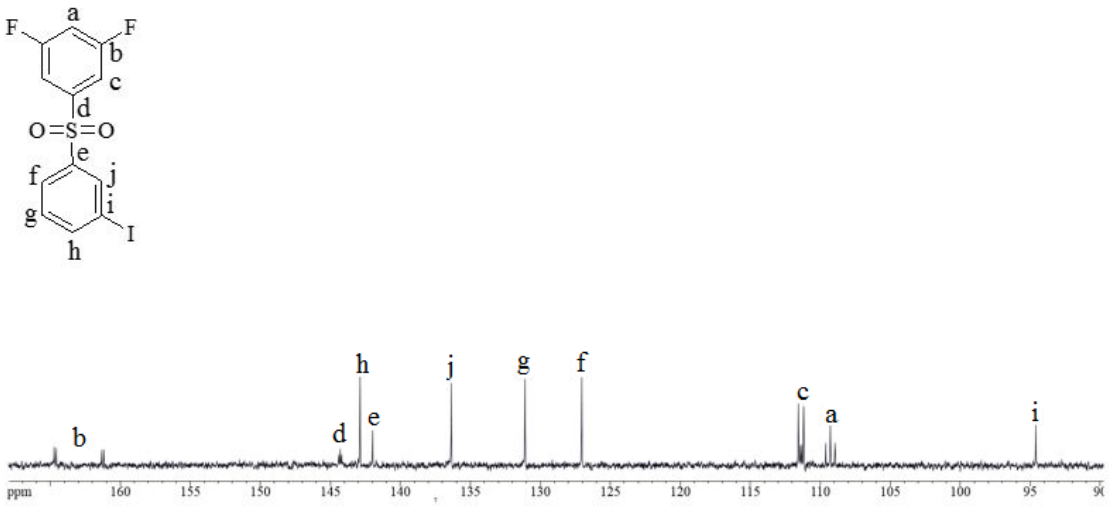


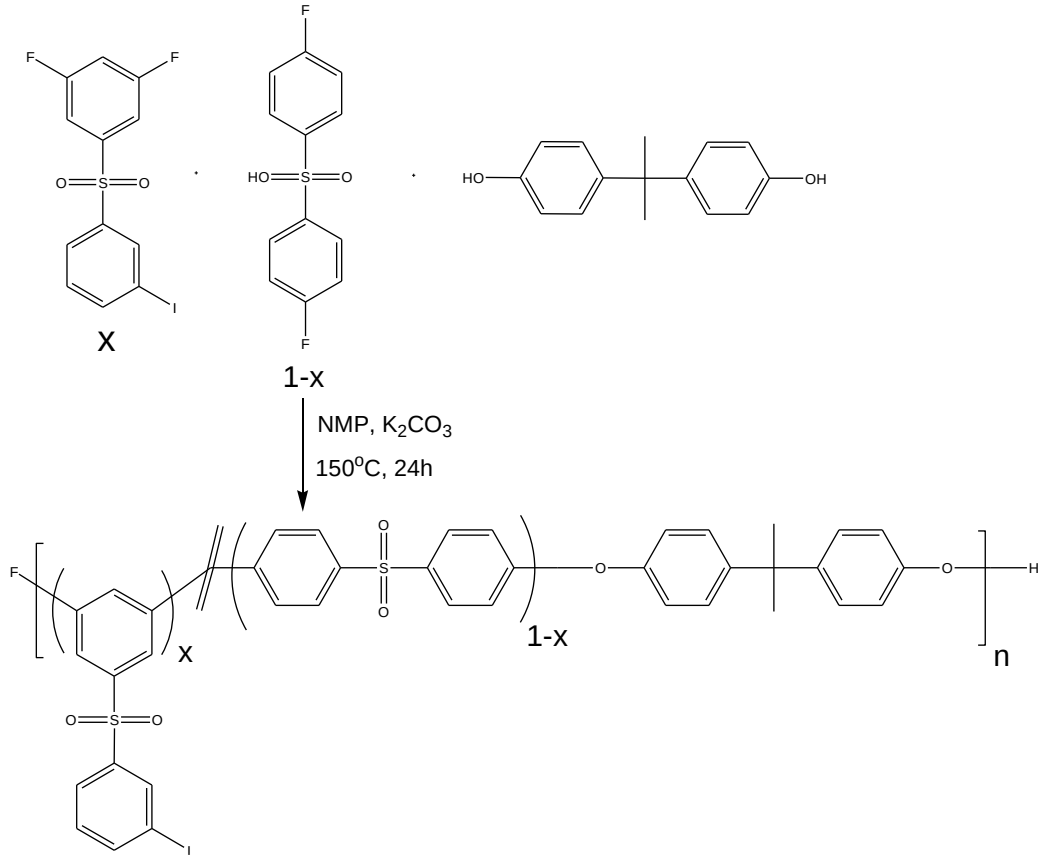
Figure 8. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **2**.

The ^{13}C NMR spectrum of **2** shows splitting in the signals of the carbons atoms present on the upper fluorinated aromatic ring of the monomer, due to carbon-fluorine coupling which results in carbon **a** appearing as a triplet at 109.4 ppm. The two equivalent carbons **b** appear as a doublet of doublets at 163 ppm, while the two equivalent carbons **c** appearing as a doublet of doublets at 112 ppm. Carbon **d** appears as a triplet at 144 ppm. All other carbon peaks of the monomer appear as singlets in the spectrum with the distinct feature as carbon-iodine (C-I) resonance peak appearing as a singlet at 94.8 ppm.

3.2. Polymerization of Iodo monomer 2 to Iodo Copolymer (25%) 3:

The iodo copolymer **3** was successfully synthesized by reacting monomer **2** with the comonomer, 4,4'-DFDPS, and Bisphenol A in the ratio 25:75:100, in the presence of K_2CO_3 in NMP at 150^o for 24 h (**Scheme 21**). The reaction mixture was precipitated from water followed by first reprecipitation from methanol and again from ethanol to obtain **3**

as off white solid (76%). Polymerization conditions for **2** were followed as established and published by Tatli *et al*.[34]



Scheme 21. Polymerization of **2** to **3**.

Though the reaction was carried out at a temperature of 150^{o} with a strong nucleophile, Bisphenol A, the C-I bond remains intact as confirmed by the peak assigned to the C-I at 94.8 ppm, in the ^{13}C NMR spectrum shown in **Figure 9**. This also shows a site for "post" functionalization was successfully established. Carbons **a**, **b**, **c** and **d** were reduced into singlets due to the loss of C-F coupling and also due to the displacement of fluorine atoms by bisphenol groups. A new peak appears at 161.9 ppm, due to the formation C-O bond in the polymer backbone.

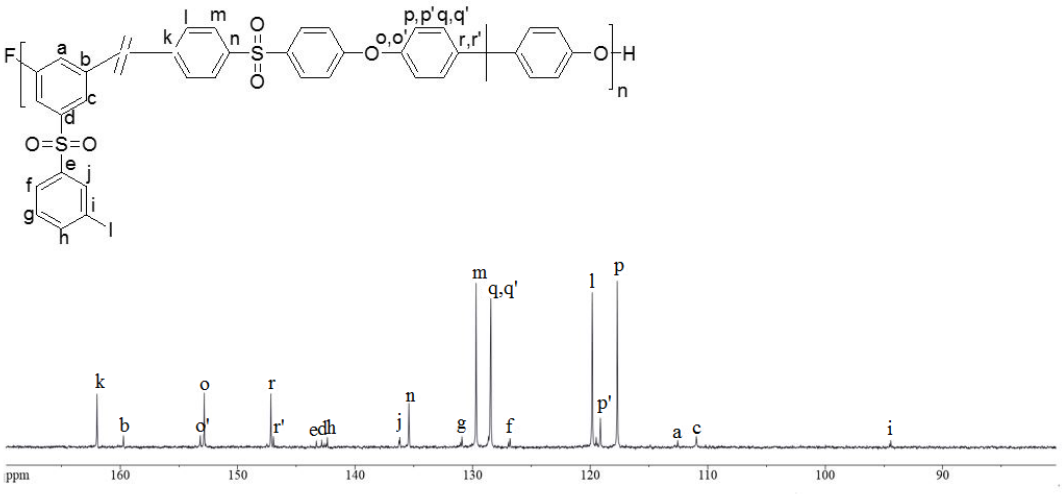


Figure 9. 75.5 MHz ^{13}C NMR spectrum ($CDCl_3$) of **3**.

The overlay of **2** and **3** is as shown in the **Figure 10**. As the concentration of the monomer decreases, the intensity of the corresponding signals also decreases. The signals **k**, **l**, **m**, **n** corresponding to the comonomer will be seen and confirmed by ^{13}C NMR spectroscopy. The successful synthesis of iodo-containing copolymer will help in the control and location of the functional groups for "post" modification.

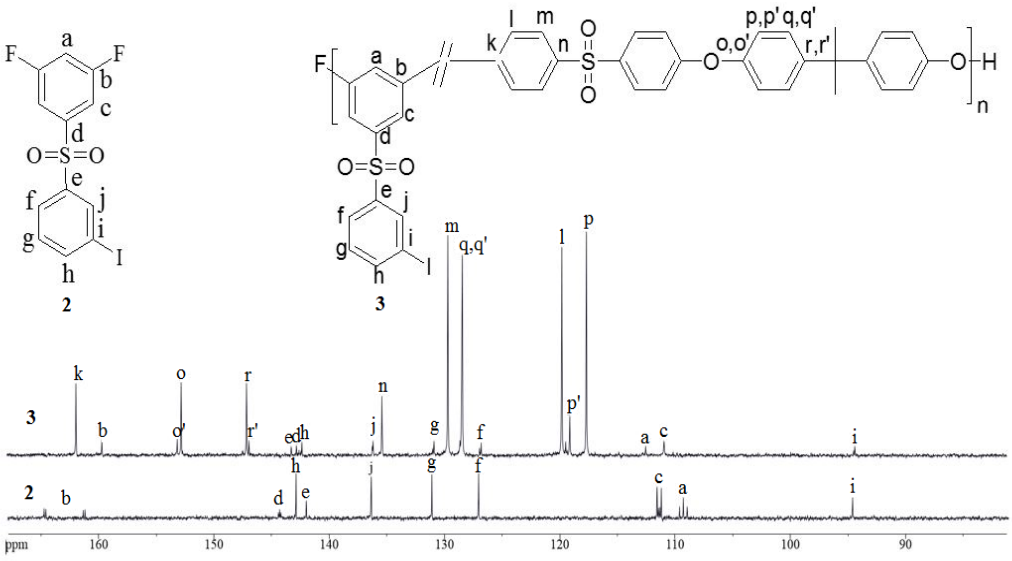
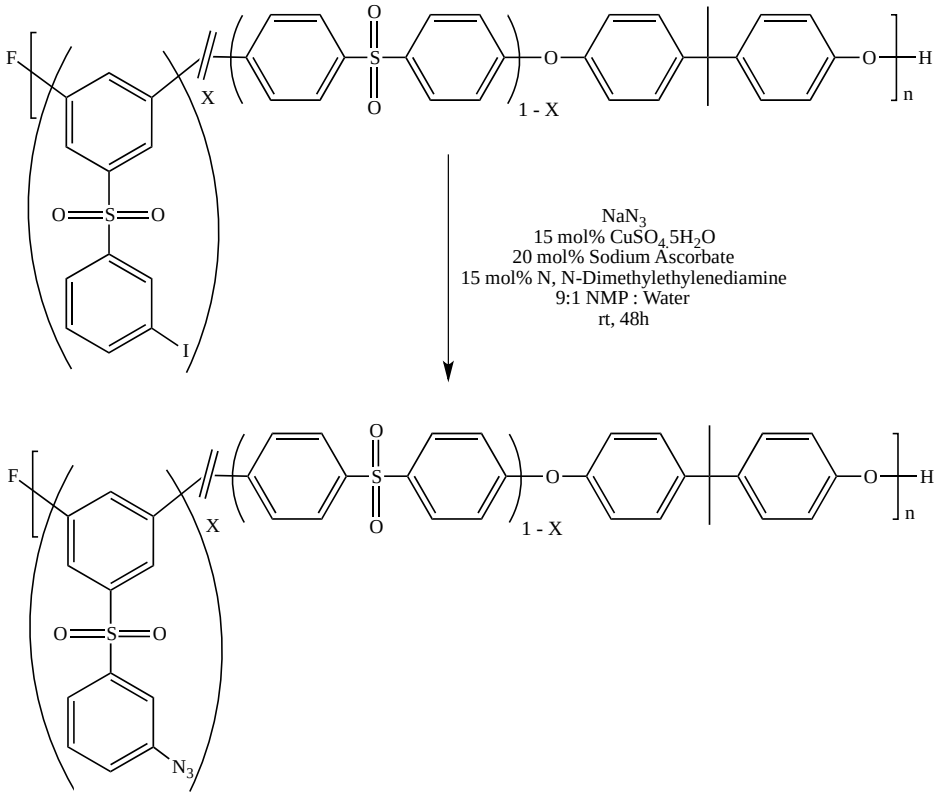


Figure 10. 75.5 MHz ^{13}C overlay spectra ($CDCl_3$) of **2** (bottom) and **3** (top).

3.3. Synthesis of Azide Copolymer 4:

Modification of an iodo group to an azide group was introduced with an aim of increasing the range of functional groups to PAES materials. The procedure for the modification of iodo group, located on a pendent phenyl sulfonyl unit, into an azide group using sodium azide and copper sulfate ($CuSO_4$) as catalyst in NMP was successfully established by Tatli *et al* (**Scheme 22**).[29]



Scheme 22. Synthesis procedure for **4**

After 48 h, the completion of the reaction was confirmed by ^{13}C NMR spectroscopy. According to ^{13}C NMR spectral data in **Figure 11**, the peak corresponding to the carbon-iodide resonance at 94.5 ppm completely disappeared and a new peak corresponding to the carbon attached to azide group was found at 141.9 ppm. The peaks corresponding to the carbons **f**, **j**, and **h** of **3** are at 128.4 ppm, 135.4 ppm, and 142.3 ppm were shifted and were observed as carbon **f**, **j** at 123.9 ppm, carbon **h** at 128.9 ppm in azide copolymer **4** spectrum. This is shown in the overlay of **3** and **4** as in **Figure 11**.

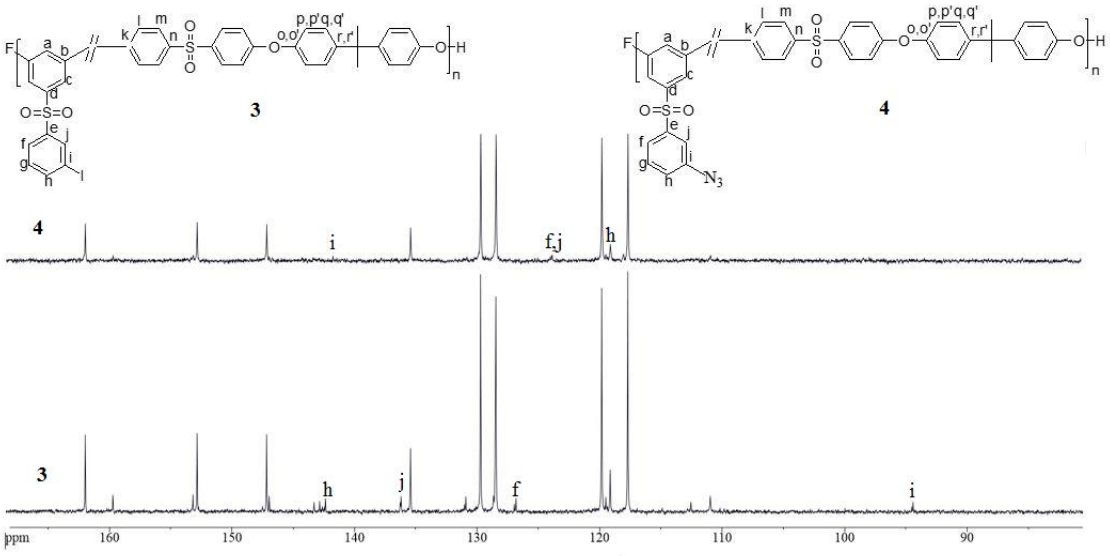


Figure 11. 75.5 MHz ^{13}C overlay spectra ($CDCl_3$) of **3** (bottom) and **4** (top).

The azide copolymer **4** synthesis was also confirmed by IR spectroscopy. From **Figure 12**, the N_3 stretch was observed at ~2111 cm^{-1} which is the reported range for absorption of $N=N^+=N^-$ group in aryl azides.

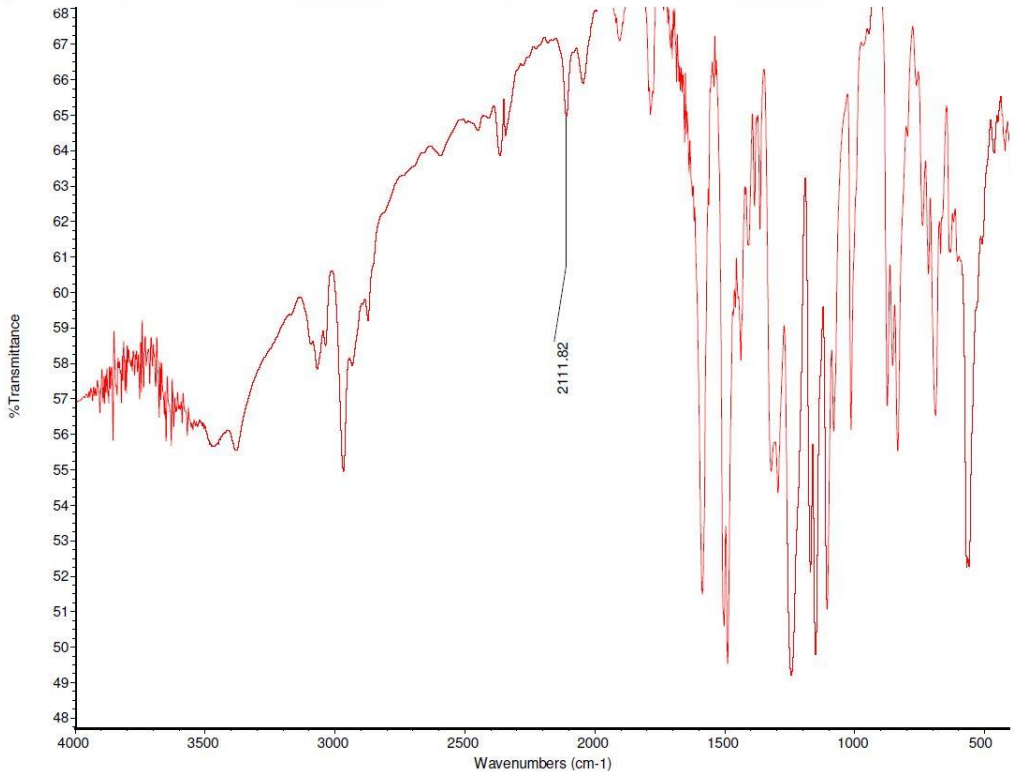
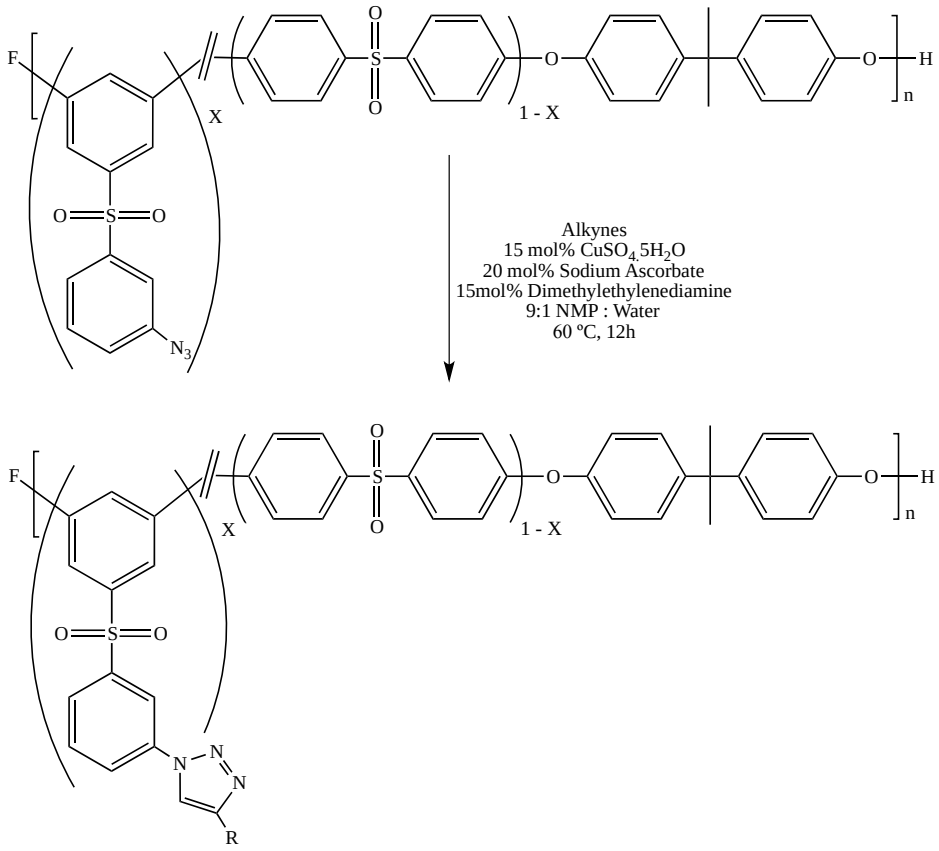


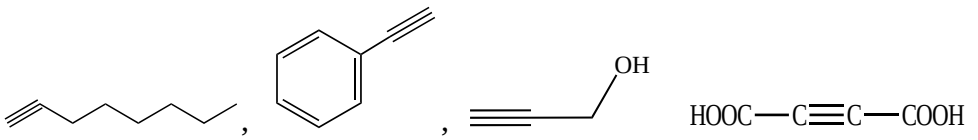
Figure 12. IR Spectrum of **4**.

3.4. "Post Click" Modification of Azide Copolymer 4 to Triazole Copolymers 5a-d:

After the successful preparation of the azide copolymer, the goal was to "click" the copolymer **4** with different alkynes to convert the azide moiety to triazole groups, using $CuSO_4$ as the catalyst in NMP at 60^o for 12 h as shown in **Scheme 23**. The polymers were precipitated from water and the completion of the reaction was confirmed by using ^1H NMR spectrum.



Where Alkynes =



1-octyne, Phenyl, Acetylene, propargyl, alcohol, acetylenedicarboxylic acid

Scheme 23. Synthesis procedure for Triazole copolymer **5a-d**.

The ^{1}H NMR spectrum of triazole copolymer using 1-octyne **5a** is shown in **Figure 13**. This shows that the regioisomers were formed. The distinct peaks of the triazole polymer represent the aliphatic protons which are labeled as **b**, **c**, and **d** appeared at 2.3

ppm, 1.27 ppm, and 0.81 ppm. The proof of the presence of the two possible structures after the reaction (**a** and **a'**) are seen at 8.2 ppm and 8.18 ppm.

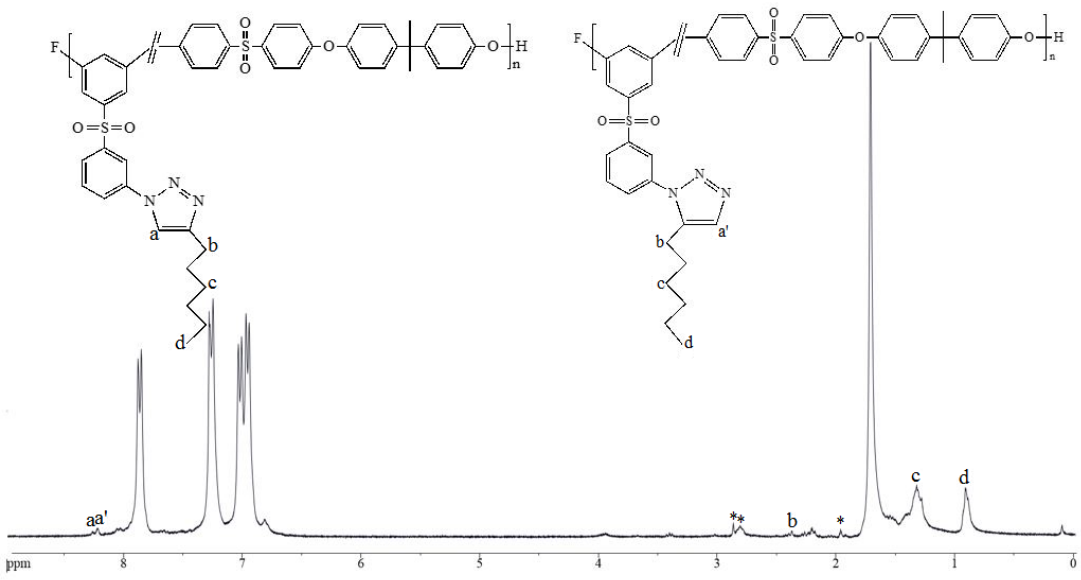


Figure 13. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **5a.**

The ^{1}H NMR spectrum of triazole copolymer using phenyl acetylene **5b** is shown in **Figure 14**. This shows that the regioisomers were formed. The distinct peaks of triazole polymer represent the aromatic protons which are labeled as **b**, **c**, and **d** appeared at 7.58 ppm, 7.45 ppm, and 7.39 ppm. The proof of the presence of the two possible structures after the reaction (**a** and **a'**) are seen at 8.35 ppm and 8.15 ppm.

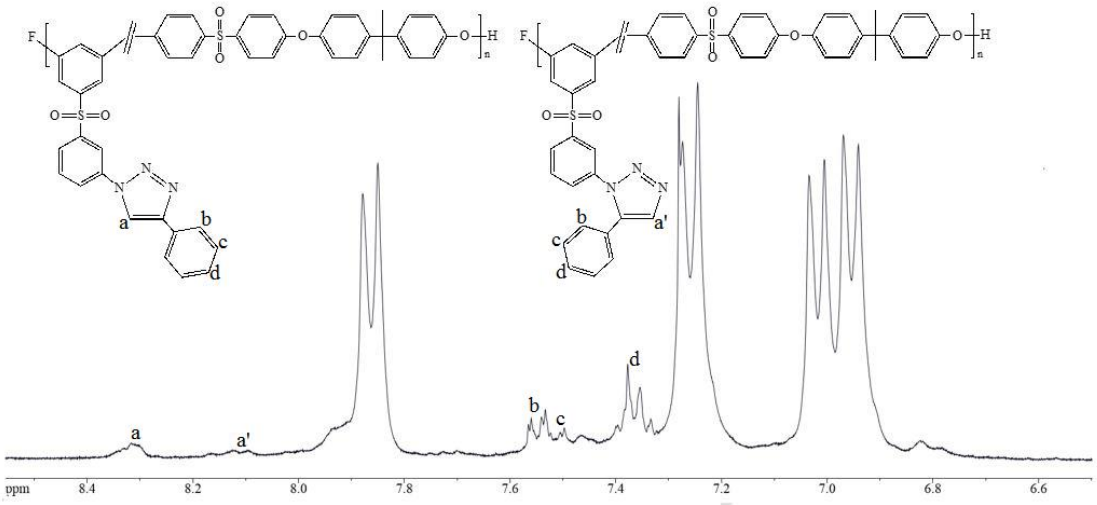


Figure 14. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **5b.**

The ^{1}H NMR spectrum of triazole copolymer using propargyl alcohol **5c** is shown in **Figure 15**. This shows that the regioisomers were formed. The distinct peaks of triazole polymer representing the aliphatic proton and alcoholic proton which are labeled as **b**, and **c** appeared at 4.38 ppm, and 1.81 ppm. The proof of the presence of the two possible structures after the reaction (**a** and **a'**) are seen at 7.45 ppm. The peak **b** at 4.38 ppm shows that aliphatic protons attached to the triazole ring and the –OH group. The intensity of the peak **b** was 0.16:1, in which propyl group of Bisphenol A was integrated to 1 as only 1:1 moles of azide to propargyl alcohol was used but if the reaction went to completion, the intensity of the peak would be 0.25:1. This ratio shows that only 70% of the azide group was converted into triazoles. However, click reactions are supposed to be quantitative or nearly quantitative. The yield and intensity of the peak can be increased by using excess of propargyl alcohol. Since the reaction has not gone to completion, the reaction time can

be increased, different solvent can be used, or the amount of the propargyl alcohol can be used in excess to increase the conversion.

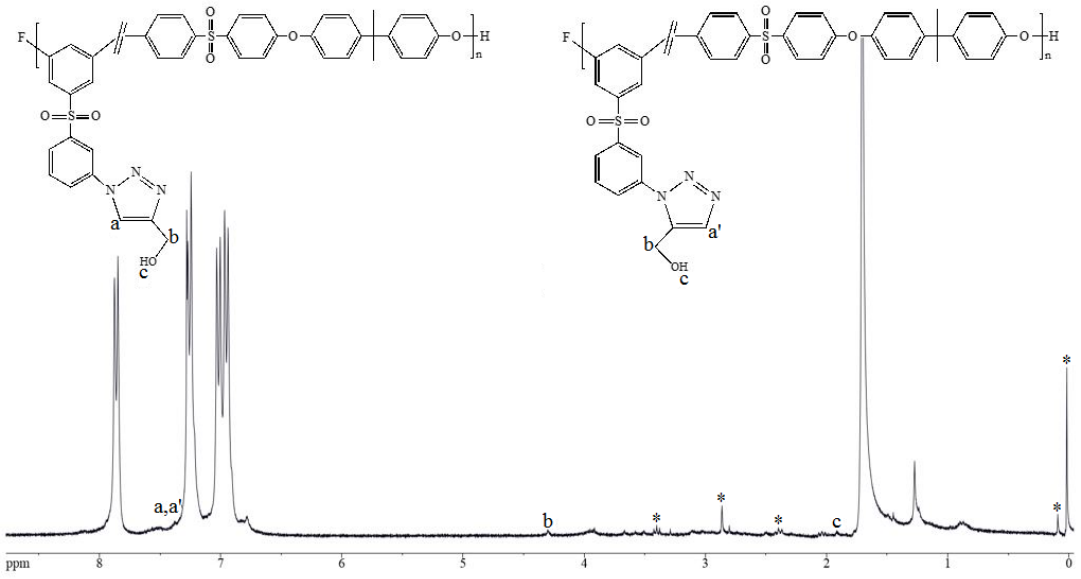


Figure 15. 300 MHZ ^{1}H NMR spectrum ($CDCl_3$) of **5c**.

The structure of **5c** was also confirmed by IR spectroscopy. From **Figure 16**, a broad spectrum for OH stretch in an alcohol was observed at 3372 cm^{-1}, a strong peak for C-H stretch of an alkane was observed at 2950.3 cm^{-1} and a strong peak for C-O bond was observed at 1050 cm^{-1}.

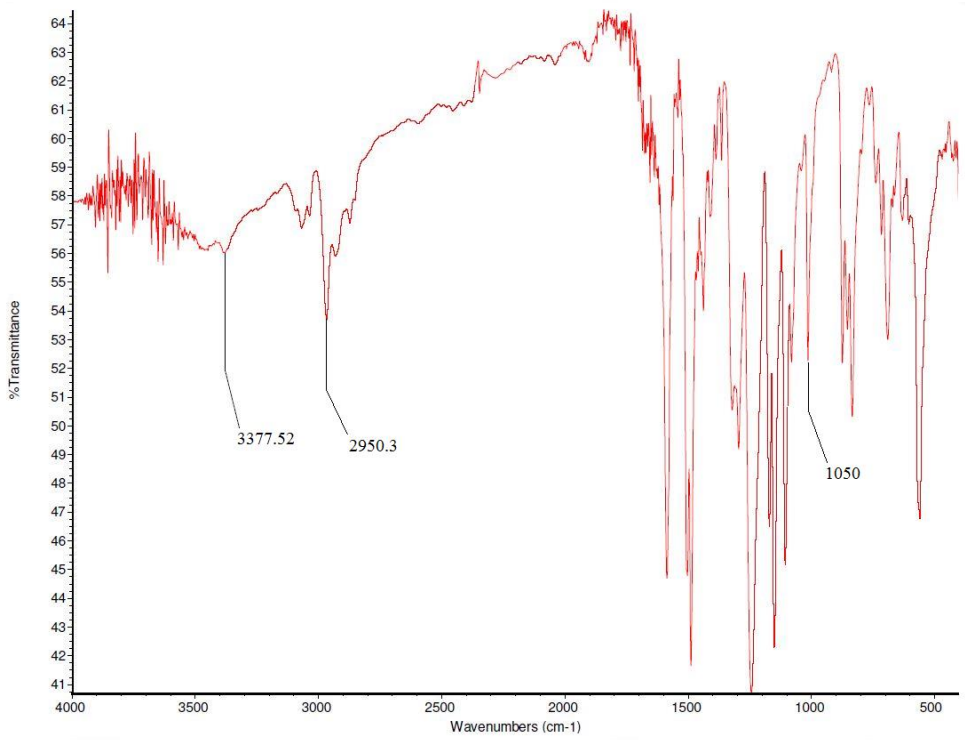


Figure 16. IR spectrum of **5c**.

The ^{1}H NMR spectrum of triazole copolymer using acetylenedicarboxylic acid **5d** is shown in **Figure 17**. There are no regioisomers with the symmetrical acetylene derivative. The distinct peaks for triazole polymer representing the polar acid protons which are labeled as **a** and **a'** were appeared at 1.82 ppm. This polymer does not contain any regioisomers as this is a bridged alkyne. The intensity of peak a and a' were less (0.13:1) as the 1:1 moles of azide and acetylenedicarboxylic acid were used and also might be due to the addition of $CuSO_4$.The ratio shows that the reaction has not gone to completion and only 55% of the azide group has converted into triazole. This copolymer can also be done using Cu-free cycloaddition reaction.

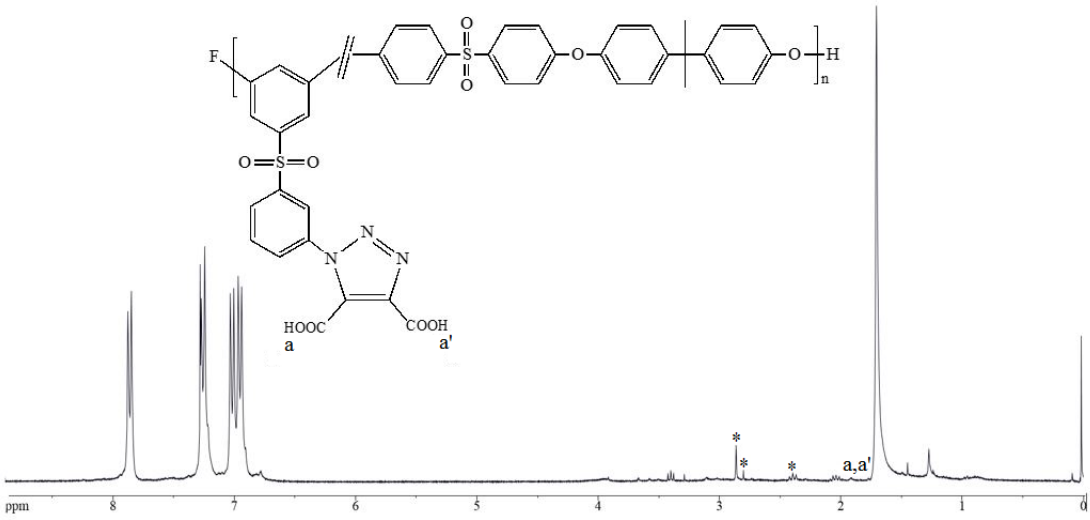


Figure 17. 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **5d**.

The structure of **5d** was confirmed by using IR spectroscopy. From **Figure 18**, a broad spectrum for OH stretch in carboxylic acid was observed at 3480 cm^{-1}, strong peaks for the C=O stretch and C-O stretch were observed at 1685 and 1050 cm^{-1}, respectively. A small peak for C=C stretch in triazole ring was observed around 1750 cm^{-1}. *'s represents the solvent peaks.

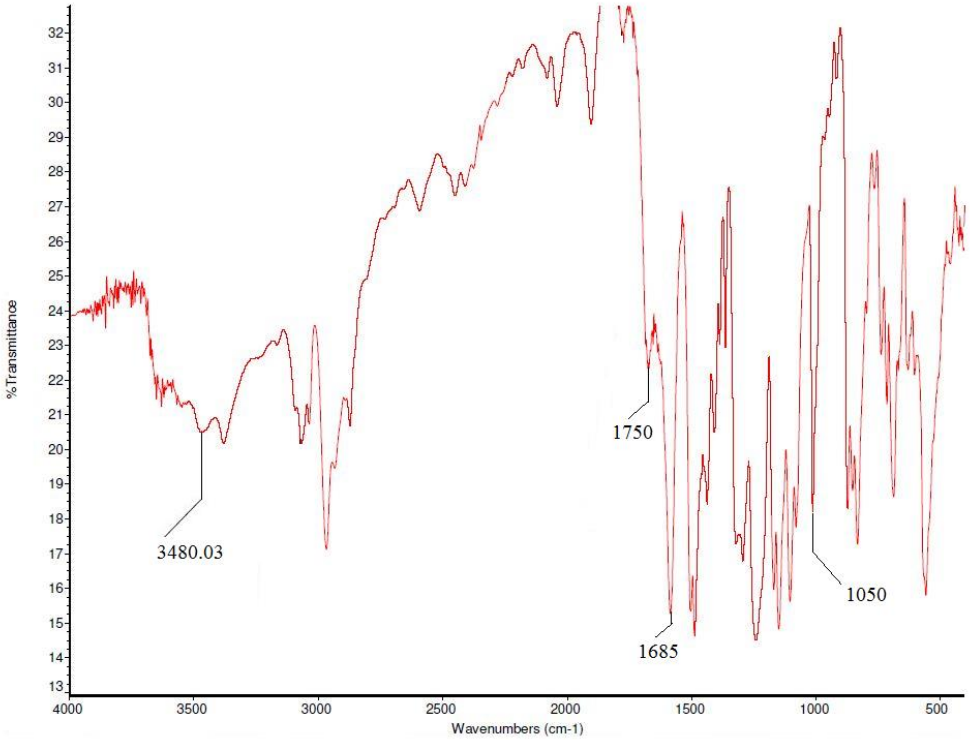


Figure 18. IR spectrum of **5d**

3.5. Polymers Characterization:

Further polymer characterization was done by using Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Size Exclusion Chromatography (SEC). Using SEC, the weight average molecular weight (M_w) and polydispersity (PDI) of the polymers were recorded as shown in **Table 1**

Table 1. Polymer Characterization Data of Copolymers **3-5(a-d)** using SEC:

Polymer	% yield	M_w (Da)	PDI
3	76	19,000	3.0
4	52	11,200	2.5
5a	58	11,000	3.3
5b	55	11,500	3.4
5c	51	7,500	2.6
5d	72	6,900	2.5

The molecular weights of the polymers **3**, **4**, and **5(a-d)** were found to be as 19,000, 11,200, 11,000, 11,500, 7,500 and 6,900 Da with the PDI values as 3.0, 2.5, 3.3, 3.4, 2.6 and 2.5 respectively. The molecular weight of **3** was found to be the highest while **5d** has the lowest. As the polymer was being modified and clicked with different alkynes, decrease in molecular weights was observed. This might also be due to the polarity of the groups attached. A hexyl group and phenyl group are relatively non-polar, thus they should have considerably different solubility than the more polar CH_2OH and carboxylic acid groups. The polymers **5c** and **5d** have less molecular weights (7,500 and 6,900 Da, respectively) as these polymers pendent groups with polar -OH and -COOH groups which will lead them to form intermolecular bonding in the molecules resulting in more cyclics in the structure of the polymers due to this chain stiffness of the backbone occurs and chain enlargement is restricted.

3.5.1 Thermal Analysis

The thermal analysis of the polymers were done using Thermogravimetric analysis (TGA) and Differential Scanning Calorimeter (DSC). The thermal properties of the polymers were evaluated and determined as 5% decomposition temperature ($T_{d5\%}$) and glass transition temperature (T_g) values, respectively, with the data being summarized in **Table 2**.

Table 2. Thermal analysis data of the polymers of Copolymers **3-5a-d** using TGA and DSC

Polymers	**$T_{d5\%}$ (ºC)**	**T_g (ºC)**
3	476	176
4	N/A	183
5a	260	174
5b	332	191
5c	308	182
5d	362	185

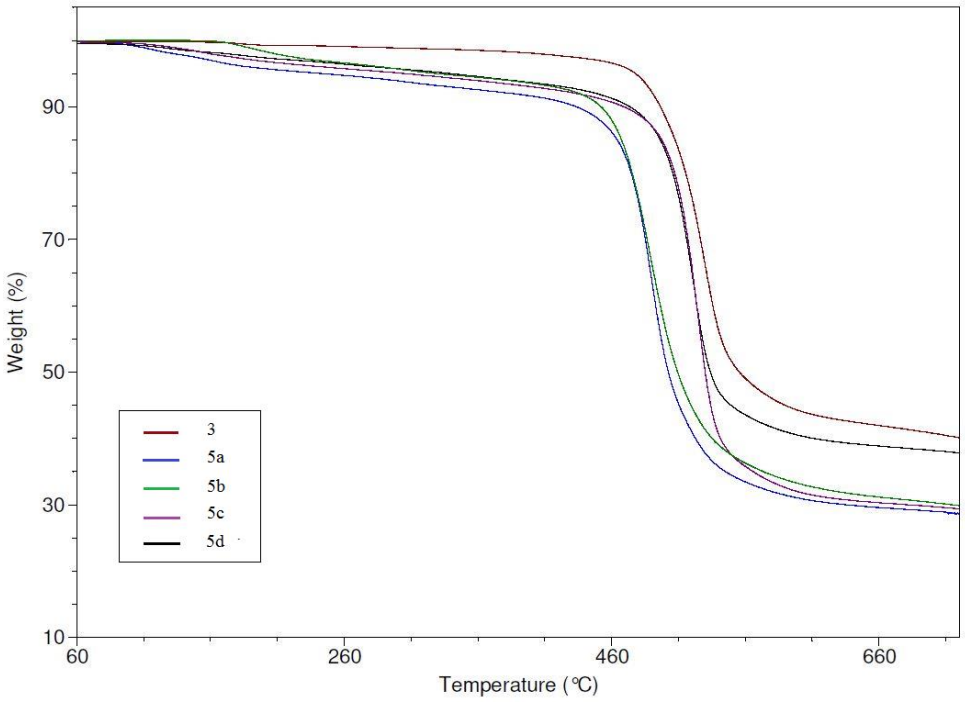


Figure 19. TGA traces of polymers **3**, **5a**, **5b**, **5c** and **5d**.

The TGA traces of the polymers are as shown in the **Figure 19.** The decomposition temperature ($T_{d5\%}$) values of polymers **3**, **5a**, **5b**, **5c** and **5d** are 476°, 260°, 332°, 308° and 362° respectively. Polymer **3** has the highest $T_{d5\%}$ value since it has Iodo group attached to it when compared to the other polymers. There is no $T_{d5\%}$ value for polymer **4** as it might contain small traces of copper azides, which are explosive and might damage the instrument. Polymer **5d** shows highest $T_{d5\%}$ value 362° when compared to polymers **5a, 5b, 5c** as it is attached to polar carboxylic acid groups while **5b** shows the next highest $T_{d5\%}$ value of 332° as it is also attached to aromatic phenyl group. The polymer **5c** shows the $T_{d5\%}$ value of 308° as it contains polar hydroxyl group when compared to that of **5a** which shows the least $T_{d5\%}$ value of 260° as it contains the long alkyl chain in the series of

the polymers. The thermal stability of a material is determined by its structural components, which may depends on aromaticity and polarity of the compounds.

The glass transition temperatures (T_g) of the polymers were determined and the corresponding DSC traces are shown in **Figure 20.** Polymer **5b** shows the higher T_g value, 191^o, as it has the phenyl group attached to it while the remaining polymers also shows the T_g values closer to it and the least T_g value was observed in the polymer **5a** of 174^o as it has the long alkyl chain. Polymer **3** shows a higher T_g value was 176^o as it has bulkier iodo group. Polymer **4** has a T_g 183^o as due to the polar azide group attached to it. Polymer **5d** has a highest T_g of 185^o and polymer **5c** has a T_g value 182^o as these have polar groups attached to it. It would be expected that the **5d** has highest T_g when compared to all other polymers because of the decrease in the concentration of the triazole moiety when compared with comonomer and Bisphenol-A. The high Tg would more likely be a result of the strong H-bonding from the carboxylic acid groups.

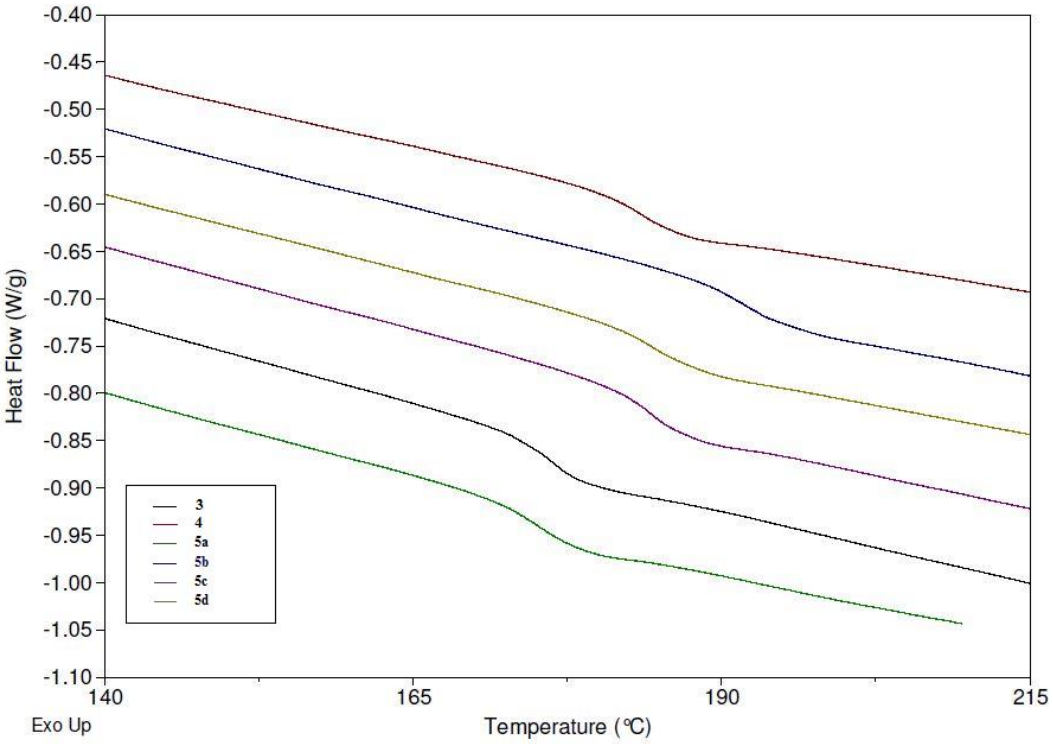


Figure 20. DSC traces of polymers **3**, **4**, **5a**, **5b**, **5c** and **5d**

4. CONCLUSIONS

Synthesis of the iodo monomer **2** and polymerization of the corresponding iodo copolymer **3** were successfully achieved. The ratio of the monomer was decreased to 25% in order to control the location of the functional group attaching it. Azide modification of iodo copolymer was done in order to allow the facile modification of poly(arylene ether sulfone) and the azide copolymer **4** was successfully synthesized, providing the site for future modification using different functional groups. The azide functional group was introduced and "post click" modification was done on this using alkynes such as 1-octyne, phenyl acetylene, propargyl alcohol and acetylenedicarboxylic acid to produce a series of functionalized copolymers **5a-d**. The introduction of the different functional groups at the same position will modify the physical and chemical properties of the copolymers without altering the backbone. The polymers showed good solubility in THF, chloroform, DCM, DMAc and NMP but were insoluble in methanol, ethanol, DMSO and hexane. The successful synthesis of the copolymers **3**, **4**, **5a-d** were confirmed by using ^{1}H and ^{13}C NMR spectroscopy. The azide copolymer **4** was confirmed by IR spectroscopy. The structure of triazole polymers **5c** and **5d** were also confirmed using IR spectroscopy. The thermal properties of the copolymers were also analyzed and recorded as glass transition temperature (T_g) and as 5% decomposition temperature ($T_{d5\%}$), using DSC and TGA respectively. The $T_{d5\%}$ values are in range of 260^{o} to 476^{o} for polymers **3**, **5a-d**. It was concluded that more the aromatic and polar groups attached highest will be $T_{d5\%}$ values. Using the DSC, T_g values are in range of 174^{o} to 191^{o} for polymers **3**, **4**, **5a-d**. It was observed that the more aromatic polymers, (such as phenyl acetylene) and the polarity of the polymers exhibited higher T_g values.

5. FUTURE WORK

Polymers containing aryl iodo groups can be modified by different halides and alkyl chains, via "post" modification, to observe how various groups will alter the physical and chemical properties of the polymers. The halide groups should be modified with azides. The azide polymers should be should be further modified with different varieties of alkynes using Cu catalyzed click modification and also several studies were proposed to modify using Cu free Click modification. The characterization of the polymers should be evaluated using TGA, DSC, ^{1}H, ^{13}C and FT-IR spectroscopy.

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